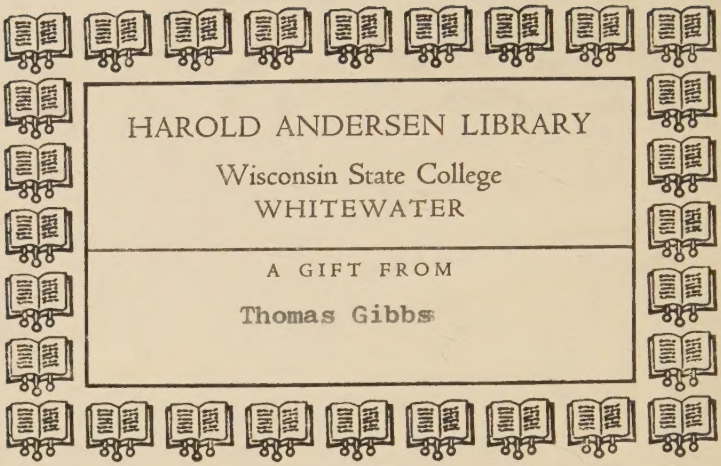
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THE INDUSTRIAL USES OF BAUXITE

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THE INDUSTRIAL USES OF BAUXITE

WITH AN ACCOUNT OF ITS ORIGIN, OCCURRENCE, COMPOSITION AND PROPERTIES

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PREFACE

BAUXITE to-day occupies a high position amongst mineral raw materials, and it is doubtful whether any other has so rapidly increased in importance. The world production of this ore has fluctuated violently, but it doubled between the first and second quadrennial periods following the war. This striking advance was due mainly to an increase in the use of the metal aluminium, and it was very little influenced by that new application of bauxite: the manufacture of aluminous cement; yet the potential demand of the aluminous cement industry is enormous. It is limited only by the relative scarcity of bauxite and by its price.

This book aims at setting out the physical and chemical properties of bauxite and describing its various uses. It is hoped that it may serve to stimulate the search for the ore, to suggest new outlets for it, leading to a more economic exploitation of occurrences already being operated, and to acquaint existing producers, consumers and others with what is being done in the various industries in which it is used.

One chapter deals briefly with the known occurrences of bauxite. After careful consideration it was decided that a detailed account of the occurrences would be out of place here, especially as there was already a book—that of Rumbold—dealing with that matter. The decision has been further justified by the recent publication of another work—that of Fox—which deals with the occurrences in detail. The references at the end of the chapter in question, which, it is hoped, are fully up-to-date and include all important literature on the occurrence of bauxite, will enable the reader to follow up any occurrence in which he is particularly interested.

The literature relating to most of the uses of bauxite is scanty. There has been a considerable number of articles dealing with the properties of aluminous cement,

but few of them are of any permanent value. On the manufacturing side practically nothing has hitherto been published.

I am indebted to a number of geologists and others for information on occurrences of bauxite and other matters, and reference to these authorities is generally made at the end of the appropriate chapter. Special thanks are due to Dr. P. H. Bates of the U.S. Bureau of Standards, whose pioneer work on aluminous cements remains unrivalled, for information kindly supplied. I would also mention Messrs. The Lafarge Aluminous Cement Company of London, and The Atlas Lumnite Cement Company of New York, who kindly supplied information on the properties of their products.

N. V. S. K.

LONDON, *May*, 1928.

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CHAPTER I

INTRODUCTION

Definition

FOR the purpose of this book " bauxite " may be defined as any rock containing free hydrated alumina in quantity. Bauxite is not a mineral species. In general it is considered to be a mixture of gibbsite ($Al_2O_3.3H_2O$) and diaspore ($Al_2O_3.H_2O$), and frequently it is classed as an aluminous laterite. The above definition covers not only the ores ordinarily classed as bauxites but also the diaspore clay of Missouri, which will, however, be called " diaspore," when it is referred to in the text.

Importance of Bauxite

Twenty years ago bauxite was unknown to most people and comparatively unfamiliar even to geologists and mineralogists. Only those interested in the manufacture of aluminium and possibly sulphate of alumina made a special study of it, and at that time the aluminium industry was not of the first importance. To-day the aluminium industry ranks high amongst the metal industries, and its importance is growing more rapidly than that of any other. Moreover, bauxite is now being employed as a raw material in a number of other industries of considerable importance and public interest. It is therefore much better known than it was and it is being actively sought by prospectors in many lands, with considerable success.

In spite of extensive research on the use of other raw materials bauxite remains to-day the almost exclusive source of the alumina used in aluminium manufacture. Quite apart from its other uses, therefore, the demand for it will increase rapidly, and as the occurrences at present being

worked are exhausted—and few of them are of great extent—the commercial value of other sources of supply will increase, and bauxite at present too remote from a market for successful exploitation will doubtless be developed. Furthermore, the newer uses of this material, which are increasing rapidly, furnish a market for bauxite in countries too far removed from the cheap water power necessary for the production of the metal, and these other uses also furnish a market for bauxite which owing to its impurities is not suitable for that purpose.

Bauxite is therefore an important raw material in several industries, and a supply of it of suitable quality is a matter of national importance : a fact fully realised by the Central Powers during the war. It is evident that with the growth of the various industries its importance will increase, and as long as supplies are unexhausted it would seem probable that it will maintain its place in competition with other sources of alumina. With minor exceptions discussed in Chapter XV the cost of treating all other materials for the production of alumina has so far proved too great to warrant their industrial use for this purpose, and although with the beginnings of the exhaustion of the bauxite supplies processes of using other materials will doubtless be employed, their cost will probably always leave a wide margin in favour of bauxite, so that it will continue to command a good price.

Historical

Although alum, now a product of bauxite, has been known and used from the earliest times, it was not formerly made from this material, and bauxite has been known only for about a century. It was discovered, or rather first recognised as distinct from ordinary clay, by Berthier [1] at Les Beaux or Baux in Provence, France : hence the name " beauxite," proposed by Dufrénoy and afterwards changed

to "bauxite" at Deville's suggestion. Berthier analysed the red non-plastic clay-like material found there and showed that it was practically free from silica and contained over 50 per cent. of alumina.

Diaspore, the crystalline monohydrate, was recognised at an earlier date and it seems to have been first described and named by Haüy in 1801,[2] whilst its chemical composition was ascertained by Vauquelin.[3]

The native trihydrate was first described in 1820 by Dewey,[4] who called it Gibbsite, but later on the same mineral was called Hydrargillite by Rose,[5] a name proposed by Davy [6] for a mineral which he thought was the trihydrate but which was afterwards shown to be a phosphate. Both names are still used for the mineral, but that of American origin, Gibbsite, is the more common.

Diaspore is rhombic, but recently Walther [7] has described what appears to be a different (monoclinic) form of the monohydrate, which he calls Kayserite. Furthermore Boehm,[8] in an *X*-ray examination of bauxite, identified another crystalline form of the monohydrate, which has been further identified by de Lapparent,[9] who proposes for it the name Boehmite. It is orthorhombic.

It is said that bauxite was used in Andalusia many years ago for making terra-cotta ornaments, but it became of commercial importance only when the process of making the metal had been perfected. Davy, electrolysing alumina melted in potash, obtained an alloy of the two metals but could not isolate pure aluminium. He proposed the name "aluminum" which has been revived and generally adopted in America in recent years. Deville obtained the metal by reacting on the chloride with sodium and he had previously [10] come very near to obtaining it by the modern method. He electrolysed a solution of alumina in sodium and potassium fluorides but with the proportions he employed obtained only sodium. Aluminium was first produced in 1856, but it was not until about 1890 that notable

quantities were made and from then may be dated the industrial importance of bauxite.

Bauxite was long thought to be a mineral species of the composition $Al_2O_3.2H_2O$, and although the similarity of some varieties of the ore to laterite had previously been noted it was not until 1898 that Bauer [11] showed definitely that some bauxite is to be considered as aluminous laterite. The French bauxites, however, which for long were the most important commercially, are not of this class, and it is probably for this reason that the term " bauxite " continued to be used in the sense of denoting a mineral. The French and other Mediterranean bauxites are considered by many authorities to be a variety of " terra rossa," and it is fairly generally considered that there are at least two types of bauxite, aluminous laterite and aluminous terra rossa. It is certain that most if not all bauxites are not distinct minerals. It has been suggested [12] that the term " bauxite " should be reserved for the monohydrated forms, the more highly hydrated ore being termed " laterite," but this would lead to confusion and there is no sound basis for any such division into two classes.

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CHAPTER II

ORIGIN, MODES OF FORMATION AND OF OCCURRENCE

Forms of Bauxite

BAUXITE occurs in a variety of forms suggestive of different modes of formation. Perhaps the most widely distributed form is aluminous laterite : a laterite in which the predominating constituent is alumina. Bauxite ranges in colour from white and grey to dark red and sometimes purple, and in hardness from a soft earth or non-plastic clay to a tough and hard rock, or, on the Mohr scale, probably between 2 and 7. The colour is not a gauge of the iron content. Very frequently bauxite is pisolitic (sometimes oolitic) in structure, the pisolites generally having a concentric structure and being cemented together by a matrix which may be harder or softer and lighter or darker than the pisolites. Most bauxites are of porous texture and many have a cellular or vermicular appearance.

Some bauxites retain the texture of the rock from which they were derived : notably the " granitic " bauxite of Arkansas. They are then honeycombed or spongy. The majority, however, are too much altered to show any outward resemblance to the parent rocks. They are cellular, vermicular or pisolitic rocks of different degrees of hardness or, as in many occurrences in the south of Europe, stiff clays.

The appearance of bauxite is so varied that it is not an easy material to locate and it is very difficult to judge the quality of a sample from its appearance. Prospectors and geologists with experience of the ore sometimes learn to distinguish it with comparative ease and may form a good idea of the alumina content, but even the most experienced often err widely and an analysis is the only reliable guide to quality. The readiness with which it dissolves in hydrochloric or sulphuric acid is sometimes used by prospectors as a rough test of quality, and another rough guide is afforded by the behaviour of the dried

sample of the material when ground in a mortar (preferably of agate—the test was suggested by J. M. Hill). A good bauxite sticks to the mortar and the more combined silica there is present the less the sticking and the greater the ease of grinding.

Until recently, diaspore was merely of mineralogical interest, but it has now been found and exploited in Missouri, U.S.A. It occurs in beds of flint clay, from which it differs in being of a rough sandy texture. It varies from a hard blue or grey clay through an oolitic form to a porous mass similar to bauxite, and it forms only a small proportion of the total clay with which it is associated.[20]

Theories of Formation

The geochemistry of bauxite formation has been the subject of much speculation and there is still no general agreement about it. It is probable that there are at least two distinct processes of formation corresponding with the " laterite " and the " terra rossa " types into which some geologists [1] divide all occurrences of the ore, but the mechanism of neither has been cleared up. Many bauxites occur as aluminous enrichments in laterite and they have clearly been formed from the same parent rock. The laterite generally occurs as a capping on a kaolinised igneous rock which in turn overlies the rock itself (basalt, granite, syenite, etc.), and the aluminous enrichments often occur near the top of the laterite, whilst in some instances the whole of the latter is aluminous (bauxite). It has been noticed that acidic rocks (granite, syenite, etc.) often give rise to bauxite, whilst basic rocks (basalt, etc.) generally yield ferruginous laterite, but there are numerous exceptions and ferruginous laterite is, of course, of much more extensive occurrence than bauxite. Aluminous laterites nearly all contain a high percentage of combined water, generally in excess of 25 per cent. The bauxites of southern Europe

and a few that occur elsewhere are distinguished by their low combined water content (generally 10 per cent. to 20 per cent.) and by their being found associated with limestone. They are considered by many authorities [18] to be highly aluminous forms of " terra rossa," the red clay-like residue from the weathering of certain limestones. However, it must not be supposed that there is a sharp distinction between the two forms. On the contrary, they merge into one another and it is very doubtful whether an examination of the physical and chemical characteristics of the ores would have ever suggested a division into two types.

Some bauxites have unquestionably been derived from igneous rocks. The normal weathering of such rocks results in the production of clays which in general contain a higher alumina-silica ratio than that of the parent rock. It might therefore be supposed that bauxite formation is due merely to a continuation of the weathering action resulting in further silica elimination, but this explanation is untenable because there is no evidence that normal weathering has any such effect on clay or shale. Indeed the relatively great scarcity of bauxite shows that if it is formed by a process of weathering that process must be exceptional, not normal. There are two ultimate problems of bauxite formation, the explanation of the elimination of silica and its replacement by alumina and the explanation of the formation from the same parent rock sometimes of nearly pure alumina, sometimes of nearly pure iron oxide and sometimes of a mixture of the two.

It is not certain whether lateritic bauxite is formed directly from the parent rock or with the intermediate formation of kaolin. The parent rock under the ore is always or generally kaolinised and in some instances there seems to be a gradual transition from bauxite to kaolin. Generally, however, the transition is abrupt and sometimes (for example in the typical formation given by Fox [1]) there is a layer of material between the bauxite and the kaolin

which is higher in silica and lower in alumina than either. Hayes [2] in discussing the Arkansas bauxite points out that the syenite from which it was formed under ordinary atmospheric conditions weathers to kaolin, and this is going on at the present day. The evidence is against its having been formed from kaolin because the bauxite boulders show clearly the granitic structure of the syenite and they contain no fragments of kaolinised syenite. In general it would seem that the kaolin is not an intermediate product, but that the bauxite was formed under different conditions in the Tertiary epoch and the kaolin since then, after the special conditions which resulted in bauxite formation had been replaced by conditions the same as or similar to those of to-day.

Many theories of bauxite and laterite formation have been proposed. Walther,[3] Passarge,[4] and others have suggested that the relatively high content of nitric acid of tropical rainfall may be related to the fact that large deposits of bauxite are confined practically to tropical and subtropical regions. It is suggested that the acidic water dissolves the alumina from the parent rock, and that it is reprecipitated either by the action of limestone or on the evaporation of the solution. Coquand,[5] Augé [6] and Meunier [7] all regard the French bauxites as deposits from thermal waters. They rest on corroded limestones, which are assumed to have been instrumental in precipitating the alumina from its salt form in the water. Hayes [8] attributes the formation of the Georgia, Alabama and Tennessee bauxites to a similar action, namely the action of heated ascending waters which first attack the pyrite in a shale, oxidising the sulphur to sulphuric acid. This in turn dissolves the alumina in the shale, the solution coming to the surface and being precipitated by limestone. There is no limestone present to permit of a similar explanation for the Arkansas ore, which, moreover, exhibits the granitic structure of the underlying syenite explicable only if the bauxite

was formed *in situ*. Williams [9] suggested that the Tertiary sea came into contact with the still hot syenite and dissolved the alumina, which was precipitated after evaporation, but this also fails to account for the granitic ore. Hayes [2] adopts the conception of an alkaline or saline sea coming in contact with heated syenite, but suggests that the action of the hot solution was first to dissolve the entire rock constituents, alumina and silica both going into solution. On further contact with the solution there would be a tendency for the more acid silica to dissolve further with precipitation of the less acid alumina, which would therefore replace silica in the rock. Nelson [10] has shown that tannic acid will precipitate alumina from a sulphuric acid solution of some possible parent rocks. Maclaren [11] and Campbell [12] also lay stress on upward moving subterranean waters and the latter suggests that alkali carbonates may be responsible for the dissolution of both alumina and silica with subsequent precipitation of the less soluble alumina.

Mead,[13] Holmes,[14] Woolnough,[15] Fox [1] and others consider that lateritic bauxite is formed by the sub-aerial weathering under monsoonal conditions (alternate wet and dry seasons) of a porous rock of the right composition forming a level or nearly level land surface. Opinions differ as to whether the land surface must be high or low lying. This, however, is little more than a statement of the conditions assumed to be necessary for bauxite formation and the mechanism of the process still requires explanation. It has been suggested [1] that the passage of water containing carbonic or nitric acid through the porous rock will set up a potential gradient through the rock (electrical endosmose) and this being established the phenomena of cataphoresis comes into play, the silica travelling downwards and the iron oxide upwards, the alumina gel remaining as the diaphragm. Apart from the fact that the mere soakage of water through the rock would produce only an

infinitesimal potential gradient, this introduction of colloidal phenomena does nothing to elucidate the matter. It is still necessary to explain the separation of the silica, in colloidal or true solution, from the alumina, remaining undissolved (or as a gel) and forming the diaphragm, and if that can be accounted for it is quite unnecessary to introduce electrokinetic conditions to explain the washing out of the silica and the remaining behind of alumina. Furthermore, the limonite covering or *cuirasse de fer* so often found at the surface (and sometimes in layers throughout the mass) of bauxite is just as easily explained by ordinary capillary action as by cataphoresis. Again, the conditions which are assumed to cause this separation can hardly be termed exceptional and if the electrokinetic explanation were correct bauxite and laterite should be more widespread. Finally, there is no attempt to explain the formation of ferruginous laterite alone in some parts and bauxite in others, from the same parent rock.

This failure to explain the segregation of iron oxide and alumina is shared by all the foregoing theories and it is difficult to conceive of a chemical or physico-chemical process which would result in the separation often met with in lateritic bauxite occurrences. It is therefore natural to turn to an agent whose activity is known to be specific for a possible explanation. Passarge [4] would seem to have been the first to suggest that the activity of micro-organisms might be of importance in bauxite formation, and Holland [16] developed the idea. He pointed out that many organisms require silica and probably they have the power of separating it from the alumina which they do not require. The silica is assumed ultimately to be washed out by atmospheric agency. Any theory that introduces a living agency is supported by the well-substantiated fact of the ore's occurrence in hot wet climates, and it would seem that geologists have given it too little consideration. A large number of organisms is known which have the power of abstracting

iron from water and collecting it on their surfaces. This property is shared by a large class of bacteria and by a number of protozoa, algae and fungi, and it is considered probable that these organisms may have played an important part in the formation of many deposits of iron ore. Ellis [17] has shown that fossil iron-secreting thread fungi occur in an oolitic limonite, and bog-iron ore is almost certainly formed through the activity of iron bacteria. It seems possible that similar alumina-secreting organisms may exist or may have existed in the Tertiary age. It has been objected that no organic matter is found in some bauxites, but others certainly contain it and it is not surprising that all organic remains should have been oxidised and washed out of so porous a rock.

If the term " terra rossa " can correctly be applied to them the Mediterranean bauxites are residues from the weathering of limestones. It is still necessary to account for the elimination of silica which is nearly always present in the limestones in greater quantity than alumina. The pisolitic nature of some of the ores seems inconsistent with their being simply residual deposits and it lends support to the supposition that the limestone acted merely as a precipitant, not as the source of the alumina in the bauxite. The low combined water content of the Mediterranean bauxites has not been explained. It lends support to the theory of a different origin of these ores, but too much importance must not be attached to it because they are older than most of those which are obviously lateritic and they may easily have lost water since their formation.

To sum up, the mode of formation of bauxite is still obscure. Perhaps the most attractive theories chemically are that which attributes formation to the dissolution of silica and alumina in alkaline or saline waters followed by the reprecipitation of alumina, replacing silica, on continued contact of the water with the parent rock, and that which postulates solution of alumina in acidic or saline

water and reprecipitation in contact with limestone or simply on evaporation. The former theory would apply to laterites and possibly the precipitation of iron oxide in some places and alumina in others may be due to a difference in the composition of the solvent waters. Both actions may take place in the same ore occurrence, the former action producing the granitic or vermicular ore which may be subject to solution and reprecipitation (on evaporation) rendering the upper portions pisolitic.[13] However, much more data are necessary before a decision can be reached on the chemical theories or on the possible rôle of micro-organisms in bauxite formation.

Modes of Occurrence

The known bauxites are all of Tertiary age with the possible exception of some of the French ores, which are thought to be Cretaceous. It is possible that bauxite has been formed since the Tertiary age and even that it is being formed to-day, but there seems to be no evidence for it and it is improbable that it is in process of formation to-day (see p. 16). It appears, therefore, that the peculiar conditions necessary for its formation were to be found in that age alone.

The modes of occurrence of bauxite are varied. The laterite type is often found as a capping on hills or plateaus with merely a thin covering of soil, but it may be eroded and redeposited (and even reconsolidated) and the deposit may then assume many forms. The *in situ* laterite type often has a layer of hard limonite covering it, generally a few inches, but sometimes as much as three or four feet thick. Under this, with a sharp, not a gradual, transition, occurs the bauxite, which may be pisolitic near the surface, but is more often granitic and spongy lower down. Under the bauxite there may be a soft laterite or, more often, lithomarge and the transition from hard bauxite low in

silica to soft lithomarge with upwards of 30 per cent. silica is often abrupt. Such are the primary or *in situ* bauxites of Arkansas, India, British and Dutch Guiana and many other countries. Detrital bauxite derived from this primary lateritic ore may often be in bedded masses, as in Arkansas, or in lenses, etc. As would be expected it is frequently closely associated with other sedimentary deposits and separation is often a difficulty.

The Georgia, Alabama and Tennessee bauxites are generally large lenticular pockets of nodular or pisolitic material associated with lithomarge or kaolin and often overlain by Tertiary sands and clays. The pockets follow lines of fault.

In France the occurrences are generally stratified and often they are intercalated with lacustrine deposits, but the beds have been much folded. Generally the ore lies unconformably on Jurassic or Cretaceous limestone and it is sometimes overlain by deposits of Cretaceous limestone. Many of the deposits are large and remarkably uniform in composition.

There are innumerable minor differences in the modes of occurrence of bauxite but generally they conform approximately to one of those mentioned above, which incidentally include all the most important occurrences that are at present known.

The Missouri diaspore occurs as a core in pockets of flint clay or in the form of boulders in the surface weathered clay. Commercial quantities occur in only a limited number of pits and an average pit contains only about 7,000 tons.[19, 20]

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CHAPTER III

THE OCCURRENCE OF BAUXITE

The Distribution of Bauxite

BAUXITE occurs in all the continents with the exception of the antarctic land mass, but large occurrences are rare in temperate climates. The important European ores are distributed along the lands north of the Mediterranean from France to the Balkan peninsula and they are all fairly close to the seaboard. Taken as a whole they constitute the most important source of supply of bauxite in the world. In North America workable occurrences are confined to several of the southern states and none of those so far developed shows large reserves of high grade ore, although there appear to be considerable quantities of inferior material which may some day be used. In South America the Guiana bauxite is now a very important source of the ore for aluminium and it is highly probable that other occurrences will be found in the undeveloped tropical areas of this continent. The known bauxites of Africa occur mainly in the tropical zone close to the equator. Some of them are extensive and further discoveries may be expected. There are numerous occurrences in India and it is probable that elsewhere in tropical and sub-tropical Asia it will be found in commercial quantities. The known Australasian occurrences are small in extent and uneven in quality but very little prospecting has been done in the more favourable regions of northern Australia and New Guinea.

It is impossible here to do more than outline very briefly the important occurrences which have been reported to date. The references at the end of the chapter will enable the reader to follow up any occurrence of particular importance to him.

Africa

Bauxite is not yet being exploited commercially in Africa but there is a number of occurrences which promise to be of importance.

On the Gold Coast it has been found in Ashanti on the Kwahu plateau, where the available ore is estimated to exceed 4 million tons, and at Mt. Supirri near Sefwai-Bekwai, where no less than 50 million tons are reported, and there are other occurrences.[1]

In Nyassaland an extensive occurrence estimated at not less than 20 million tons has been found on the Lichenya plateau.[2]

Bauxite has also been reported in Nigeria,[3] Sierra Leone,[4] Tanganyika Territory,[5] and Madagascar,[6] and laterite occurs in many other parts.

Australia

Although no very valuable occurrences are known in Australia there are many small ones and the search for the ore is being actively pursued.

In New South Wales aluminous laterite containing nearly equal amounts of alumina and iron oxide and low in silica occurs at Wingello 100 miles from Sydney on the Southern main railway line. The quantity available is considerable and there are enrichments of higher grade ore. It occurs on the surface with very little overburden and it adjoins the railway. Bauxite also occurs in the Emmaville, Inverell and Tingha districts.[7]

Victoria is the only state in which bauxite is being mined at the present time. Small quantities of an ore low in iron oxide but rather high in silica occurring in Gippsland are used for the production of aluminium sulphate. Many other small occurrences are known in Gippsland and some have been opened up and supplied a few tons of ore for

refractory and other purposes, but although there is some high grade ore the quantities so far proved have been small and the quality variable.[8]

In Tasmania no ore has yet been discovered, but on account of the cheap electrical power available in that island the search for bauxite is being actively pursued with a view to the establishment of an aluminium industry there.[9]

There is more chance of valuable ore being found in the more tropical parts of Australia, but it is there that least work has been done. A low grade ore has been found in the Northern Territory but no thorough prospecting has yet been done there.[10]

In Queensland there are large areas of laterite and small quantities of bauxite have been discovered, but exploratory work is still in its infancy.[11]

In Western Australia, too, laterite is abundant forming a covering a few feet in thickness on the higher levels of the flat-topped Darling Range. It lies on kaolinised granite. It is estimated that there is at least 500 square miles of laterite, and much of it is accessible to rail. The alumina ranges from 37 per cent. to 48 per cent. in a number of localities, the most important of which are Toodyay, Wooroloo, Sawyer's Valley and Kalamunda-Walliston.[12]

No bauxite has yet been found in South Australia.

British and Dutch Guiana

The Guiana bauxites have sprung into great prominence in recent years and this country promises very soon to be the world's largest producer of bauxite for aluminium manufacture. The occurrences have been examined in detail by Harrison[13] who found the ore in many localities. It is being mined in the foothill region along the Demarara River and in the vicinity of Wisman, Christianburg and Three Friends. Bauxite has been traced from close to the Venezuelan border right across British Guiana and into Dutch

Guiana (Surinam). The largest deposits are accessible to the sea so that transport thence is cheap.

The bauxites are aluminous laterites derived from altered dolerites and hornblendic rocks, and many of them are of very high purity, the alumina being as high as 70 per cent. in one sample (which must be of a partially dehydrated rock). They have been actively developed by American interests, and recently concessions have been acquired by a British company.

The same type of bauxite is found in Dutch Guiana and it is there being developed by American interests, on the Surinam River.[14]

France

France was for long the largest producer of bauxite in the world and she has recently resumed this place. It occurs in a belt almost parallel to the Mediterranean in the Departments of Ariège, Hérault, Bouches-du-Rhône, and Var, whilst occurrences of minor importance have been reported in other districts. The most important occurrences are in Var, where the ore is obtained at Thovonet, Mazaugues, Vins, Brignoles, Cabasse, and elsewhere. It is dark red but high in alumina and suitable for aluminium. In Hérault is found the white bauxite which has been used so much for chemical purposes. It occurs at Villeveyrac and there are a number of other occurrences in that department. In Bouches-du-Rhône the ore is found at Les Baux, Mausanne and a number of other localities, and in Ariège in many districts. According to Pawlowski the ore reserves in France amount to 60 million tons.[15]

Germany

Germany is badly off for bauxite, the only occurrence of much commercial importance being that at Vogelsberg in Upper Hesse, which is of basaltic origin.[16]

Great Britain and Ireland

Bauxite occurs in Antrim, Ireland, in several localities, but although it has been mined to a considerable extent it is too impure for most purposes.[17]

In Scotland an aluminous clay occurs in Ayrshire, but it is not a true bauxite.[18]

India

Laterites are of wide occurrence in India and many aluminous enrichments are known whilst large areas have not yet been prospected. It seems probable that India will one day be an important producer of bauxite.

In Bombay presidency it occurs near Belgaum in quantities estimated at over 3 million tons, and in Kolhapur state at Radhanagri (upwards of 2 million tons), Dhangarvadi and Patagaon. Bauxite is at present produced mainly for petroleum refining at Kapadvanj in the Khaira district.

In the Himalayan region bauxite occurs in Jammu (Kashmir) in quantities estimated at over a million tons but it is high in silica. Apparently diaspore also occurs here.

In the Central Provinces in the Jabalpur district are the richest occurrences in India. They are situated at a number of points and the quantity available runs into many millions of tons. As in most Indian bauxites the titanium is high. Bauxite also occurs in the Balaghat district.

Other occurrences are in Bihar and Orissa (Palamau and Ranchi districts and Kalahandi State) and in Madras Presidency in Ganjam and Vizagapatam.[19]

Italy

Important occurrences are worked in Carniola near Lake Wochein and elsewhere and in Istria near Trieste. The acquisition of the former Austrian bauxite of Istria

has made Italy one of the most important producing countries. Bauxite also occurs in the Central Apennines. In 1926 the export of the ore was officially restricted.[20]

Jugo-Slavia

The bauxites of Croatia and Dalmatia originally belonging to Austria-Hungary are now in Jugo-Slavia. Considerable quantities are mined in Dalmatia and there are important occurrences in South Croatia. It is reported that there are large reserves of high grade ore, exceptionally low in silica, in Dalmatia.[21]

North America

Bauxite occurs in many parts of the United States but the most important occurrences are in Arkansas and Georgia. The Missouri diaspore is also commercially important.

The important areas worked in Arkansas are in Salim and Palaski Counties near Bauxite and Little Rock. Both massive and detrital ores occur. The reserves were estimated at 80 million tons in 1900, but this was probably an over-estimate, and they have been heavily drawn upon. Arkansas is easily the heaviest producing state in America but its output has been decreasing in recent years. There was a recovery in 1926 but mining of the pure ore is constantly becoming more expensive.[22]

In Alabama the ore occurs at Rock Run and Piedmont in Cherokee County, in DeKalb, Taleadga and Calhoun Counties and elsewhere. It occurs in lenticular pockets mixed with more or less kaolin. It was largely used for chemical purposes but is not worked at present.[23]

In Georgia it occurs near Rome and Cave Springs in Wilkinson County and there is a large field near Andersonville, Smith County. In America bauxite was first dis-

covered and mined in this State and it is still an important producer for the chemical trade, the output being on the increase.[24]

In Tennessee the most important deposits are in Carter County but production is now small.[25]

Bauxite also occurs in Mississippi,[26] and occurrences are reported in California.[36] Diaspore is produced in Missouri [27] and is in great demand for refractories.

In Canada the occurrence of bauxite in British Columbia was reported by Dunn,[35] but attempts to find it in payable quantities have failed.[37]

Roumania

The Roumanian bauxite area in the Bihar Mountains (Transylvania) formerly belonged to Hungary. Large reserves of rather high iron bauxite are reported on the Kiralyerdo Plateau, and they have been exploited to a limited extent.[28]

Other Countries

Bauxite has also been reported in Brazil,[29] Greece,[30] Hungary,[31] Russia,[32] and Spain.[33] It was reported that mining was to be started in Russia in 1926. There seems to be none in Japan, but diaspore has been found there.[34] Aluminous clay, but not bauxite, is known in New Zealand.[38]

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CHAPTER IV

MINING, PREPARATION AND MARKETING

The Mining of Bauxite

THE greater part of the bauxite obtained at present is mined by open cut methods and much of it is done by hand. At the large deposits the overburden is generally removed by steam shovel, the surface of the bauxite being finally carefully cleaned by hand. It is then broken up by blasting and loaded by steam shovels. Where labour is cheap hand labour is used almost exclusively, and where the ore is not sufficiently uniform or not in large enough masses mining by hand is necessary for the production of a pure ore. In some of the French mines and also in Arkansas it has been found necessary to start underground mining on account of the depth of the overburden, but this is still exceptional in bauxite mining.

There are no features in bauxite or diaspore mining that call for special mention here.[4]

In most of its uses bauxite is required in powdered form, but in some of the processes of cement and refractory manufacture it is required in 3 inch or 4 inch lumps, and when mining for these particular consumers excessive breakage of the rock must be avoided.

Concentration, etc.

A considerable quantity of good bauxite is wasted because it cannot at present be separated economically from impurities and there are also large occurrences of low grade ore which would become of commercial importance if a cheap method of concentration could be devised. Some of the American bauxite is washed to remove clay, etc., but no really satisfactory method of concentration has yet been devised. The plant used in washing is generally crude, log washers often being used. The difficulty of concentrating this ore lies in the similarity of its properties to those of clay

and other impurities which contaminate it. Nevertheless it does differ from clay in being less subject to dispersion in water, and this difference has led to a process of purification in which caustic soda or some similar agent is added to the washing water to deflocculate the clay and thus facilitate its removal in aqueous suspension.[1] It seems probable that some occurrences of bauxite could in this way be separated into a marketable ore and an aluminous clay which might be used for refractories. The process is being tested by the U.S. Bureau of Mines but apparently the results are not encouraging.[2]

It would be of considerable value in some countries if a process were available for cheaply separating bauxite from admixed limonite and hematite. In America roasting followed by magnetic separation is being tried [2] and apparently a considerable amount of the iron is sometimes removable in this way, but the process is not yet commercial.

At present the processes of concentration actually in use are practically limited to hand sorting and simple washing.

Drying

The bauxite mined generally contains anything from 15 per cent. to 33 per cent. of chemically combined water and also varying quantities of mechanically held water. To save freight it is usual to drive off some of the water at the mine. In America the ore is crushed to nut size and fed to rotary kilns fired by coal dust, where it is heated to 700° C. or higher but not above 900° C. except for bauxite for abrasives and refractories, which are " dead-burnt " at 1000° or over. Only at these high temperatures is all the water driven off. Other types of direct fired driers may be used, there being no special difficulties other than the tenacity with which the ore holds a portion of its combined water. Care is necessary in heating the ore destined for producing the metal or for chemical use because excessive heat reduces its solubility in caustic soda and other solvents.

Marketing

In the past nearly all the bauxite mines were controlled by the few great aluminium producers and therefore little of the ore came upon the ordinary mineral market, but there is now a number of independent suppliers. It is usual to sell the ore at a price per unit of alumina with set limits to the allowable percentages of impurities. It is not the total alumina, however, that is of importance to some chemical users of bauxite but the " available " or " free " alumina, and the method used for the determination of this varies. It has been proposed [3] to estimate the " available " alumina by determining the amount soluble in sulphuric acid heated to fuming, whilst the " free " alumina is determined by heating at 100° for a limited period.

The quality of bauxite required for each particular purpose is dealt with in the chapters on the uses of the ore, but some general information on the grades of bauxite at present marketed may be of value at this stage.

In France bauxite is generally divided into white and red, the former being low in iron but sometimes high in silica, and the latter generally low in silica. White bauxite of first quality, used for chemical purposes, contains at least 60 per cent. alumina and not over 3 per cent. ferric oxide. Second quality ore is less pure. Red bauxite for aluminium contains not more than 3 per cent. silica and ferric oxide not above 14 per cent., whilst the alumina exceeds 57 per cent.

American practice has been to demand an ore with not more than 4·5 per cent. silica and 6·5 per cent. ferric oxide and not less than 52 per cent. alumina for metal manufacture, whilst for chemical use the silica may be as high as 20 per cent. but the ferric oxide must not exceed 3 per cent. and the titanium must be low. If the bauxite is dried at a high temperature the alumina must, of course, be higher. In recent years bauxite with silica up to 7 per cent. has been

used in metal manufacture and an alumina less than 50 per cent. has been accepted.

The widespread adoption of such new processes of preparing pure alumina for metal production as those of Haglund and Pedersen would probably modify the allowable limits of the impurities in the ore, and if it is shown that they permit the use of bauxites higher in iron and, especially, silica than the Bayer process, that fact would be a strong incentive to their widespread use. On the other hand, the other applications of bauxite generally do not call for as pure an ore as that necessary for the Bayer process and they provide an outlet for inferior ore. At present it would seem that the most favourable method of mining and marketing the ore in most instances is to separate it into two or more grades, selling the best to alumina works and the lower grades to producers of cement, refractories, etc.

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CHAPTER V

CHEMICAL COMPOSITION

The Constituents of Normal Bauxite

BAUXITE, generally being derived from granite, syenite or other igneous rock contains the variety of elements found in those rocks but in very different proportions. The normal constituents are alumina in the hydrated form, and also combined with silica, ferric oxide in varying degrees of hydration and anhydrous, silica free and combined, titanium dioxide or its hydrate, lime, magnesia, potash, soda, manganese oxide, oxides of sulphur and phosphorus and water. Of these only alumina, iron oxide, silica, titanium dioxide and water normally occur in quantity.

Alumina

The alumina in bauxite occurs free in hydrated form and also combined with silica. Two definite hydrates of alumina are known : diaspore, $Al_2O_3.H_2O$ (15 per cent. H_2O) and gibbsite, $Al_2O_3.3H_2O$ (34·6 per cent. H_2O). In bauxite the amount of combined water varies between these two limits (occasionally it seems to have been dehydrated below the monohydrate) and consequently it is generally considered that it consists of a mixture of the two hydrates. Gibbsite has been detected microscopically in the ore but there is little evidence other than that implicit in its composition of diaspore being a constituent of bauxite. An optical examination is exceptionally difficult, because it is a mixture of isotropic substances in an extremely fine state of subdivision, nor is the evidence of the temperature of water evolution finally conclusive (see p. 46).

This latter evidence points to there being the two crystalline hydrates and also amorphous hydrated alumina present in varying proportions.

For many commercial purposes, and notably in the manufacture of metallic aluminium and its salts, it is not the total

alumina in the ore that is of importance but the amount that is soluble in the solvent used in the particular process. This " available " alumina varies considerably and it is profoundly changed by heating the ore to a high temperature (see p. 33). Diaspore and some bauxites high in alumina and low in combined water are only slightly soluble in alkali solutions and in spite of their high content of alumina they cannot be employed in the Bayer process.

The percentage of alumina in diaspore and bauxite varies from 80 per cent. downwards but a high grade bauxite generally contains between 55 per cent. and 60 per cent. and a similar diaspore between 70 per cent. and 80 per cent. The high percentage in some of the French and Italian bauxites is possible only when the water content is much less than usual.

Iron Oxide

Except possibly in a few bauxites containing organic matter and not recently exposed to weathering, this constituent is always present in the ferric form either as the oxide or as a hydrated oxide. Hematite is known to occur in some bauxites and the occurrence of limonite and other hydrates is suspected but not definitely proved microscopically. Some bauxites have the colour of ochre, which is presumably a reliable indication of the presence of the hydrated oxide limonite.

In many bauxites there is a superficial enrichment of iron oxide (*cuirasse de fer*) which hides the underlying ore, and more rarely veins of it may be encountered at irregular intervals throughout a mass of bauxite.

Bauxites are known containing all proportions of ferric oxide from practically none upwards, until the amount is so high that the rock is considered a laterite. Speaking generally it is a valueless diluent but it is a less serious impurity than silica in the majority of the uses of bauxite.

It is insoluble in the aqueous alkali which is used to extract alumina from the ore and therefore the only limit to the permissible iron oxide content in ore for aluminium, pure sulphate of alumina and sodium aluminate manufacture is that set by the cost of separating and handling the iron sludge coupled with the fact that the higher the iron oxide in the bauxite the greater is the difficulty of complete solution of the alumina. For aluminous cement a moderate amount of iron oxide, say 10 per cent. or over, is preferred and high percentages are allowable in processes in which the oxide is reduced to the metal. In abrasive production it is usual to add iron to the charge so that here again an ore high in iron may be employed, and the same thing applies to fused alumina refractories. In the ordinary type of bauxite refractories, however, the permissible percentage of iron oxide is limited by its lowering of the softening point of the refractory. In dissolving bauxite in sulphuric acid the iron oxide dissolves and in consequence an ore low in iron is preferred for making sulphate of alumina by the direct process, but in many of the uses of this chemical (e.g. in water and sewage precipitation) ferric sulphate is practically as effective as aluminium sulphate, and an ore high in iron can be used for making " alumino-ferric " for these purposes.

Cheaper methods of sludge handling and washing, such as counter-current washing in thickeners, continuous vacuum filtration, etc., are making it possible to use economically bauxites much higher in iron oxide than formerly was possible and a further development in this direction may confidently be expected.

Silica

Silica occurs both free and combined in bauxite. In primary bauxites, as would be expected, free silica is often found when the parent rock is acidic (granite, etc.) but rarely when it is basic (basalt, etc.).

The proportion of silica ranges from nearly zero up to, say, 30 per cent., above which the material is not generally considered bauxite. Bauxites merge into aluminous clays, kaolin, etc., without any sharp dividing line. For most purposes a low silica content is essential and to be of much commercial value the silica should not exceed about 10 per cent., unless the other impurities are exceptionally low.

Siliceous bauxites are used for refractories and, when low in iron oxide, for making sulphate of alumina. When the silica does not exceed 10 per cent. or 12 per cent. the ore is often suitable for aluminous cement, but other factors may reduce the allowable amount. The Pedersen process of making alumina for reduction to the metal is said to permit the use of a siliceous ore but the limits are not specified. It is certain that siliceous ores ultimately will be much more generally employed than at present.

Titanium Oxide

Titanium, as the dioxide or a hydrated oxide or possibly sometimes in the form of ilmenite, is a normal constituent of bauxite, being an important constituent of the parent rocks. There is no certain evidence as to its condition in bauxite, but the hydrated form is generally favoured.[15] Though occasionally low (e.g. in some of the British Guiana bauxites) it generally ranges from 2 per cent. to 4 per cent. of the ore, and in certain instances, and notably in the Indian bauxites, it is much higher, 6 per cent. to 12 per cent. and sometimes even more. In diaspore it is generally 4 per cent. to 5 per cent.

Titanium oxide is at present a useless diluent of bauxite. Its effect on the product in those uses of the ore where it is not eliminated in the process of manufacture has not been elucidated, but in the proportions in which it is generally present it would seem that it certainly is not harmful. In making pure alumina the titanium is eliminated in the iron

oxide sludge and it is highly probable that this will become an important source of titania for paints and other applications, especially when the titaniferous Indian bauxites come into more general use (see also p. 61).

Water

The combined water in bauxite varies widely, being as high as 35 per cent. in some pure ores from Guiana and as low as 12 per cent. in equally pure French ones. A low water content, however, is unusual except in the Mediterranean bauxites and it is usual to find 25 per cent. to 30 per cent. in an ore with 55 per cent. to 60 per cent. of alumina. As the iron oxide increases (replacing alumina) the water content diminishes and siliceous bauxites also are inclined to have less combined water. The percentage of water in diaspore is generally 12 per cent. to 15 per cent.

On heating bauxite the water is evolved over a wide range of temperatures and dehydration is not complete until about 1000° C. is reached (see p. 46).

Other Constituents

Of the other constituents of bauxite, lime and magnesia are the only ones that often occur in more than traces, but the amount is seldom, if ever, enough seriously to dilute the ore. Silver, gold and tin are reported to occur in different bauxites and it is suggested that they may be recovered from the residues from the extraction of alumina from the ore.

Analyses of Typical Bauxites

The analyses in Table I have been selected from the large number of analyses available in the literature of the subject. Generally they are fairly representative of the ore available in the different countries and in several instances the average of a number of analyses is given.

TABLE I

Country	Africa	Australia			British Guiana	France (Var)	
District	Gold Coast. Mt. Ejuanema [1]	N.S.W. Wingello [2]	Victoria. Boolarra [3]	W.A. Wooroloo [4]	Christianburg [4]	Thoronet [5] (red)	La Caire [5] (white)
Alumina Al_2O_3 . .	60·6	37·3	46·9	43·4	67·3	66·2	54·4
Iron Oxide Fe_2O_3 .	9·8	29·4	15·2	17·7	1·5	19·3	0·3
Silica SiO_2 . . .	1·4	9·1	4·5	13·4	2·9	0·9	26·7
Titania TiO_2 . .	2·2	—	5·1	1·5	1·1	0·9	2·9
Water H_2O . . .	25·6	20·7	26·1	24·0	27·5	12·4	15·7

Country	Germany	Ireland	India	Italy	Jugo-Slavia	North America		Roumania
District	Hesse [6]	Antrim [7] Irish Hill	Central Provinces. Jabalpur [8]	Carniola [9]	Dalmatia [10]	Arkansas [11]	Central Georgia [12]	Bihar [13]
Alumina Al_2O_3 . .	53·1	50·7	60·5	63·1	56·3	59·8	56·7	58·7
Iron Oxide Fe_2O_3 .	10·6	7·1	2·7	23·6	22·0	2·1	1·6	25·9
Silica SiO_2 . . .	4·9	10·4	2·0	4·2	0·9	5·7	12·4	1·2
Titania TiO_2 . .	2·8	5·4	8·5	—	2·9	1·9	1·6	2·7
Water H_2O . . .	27·8	25·6	25·0	8·3	17·9	30·5	27·6	11·7

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CHAPTER VI

PHYSICAL AND CHEMICAL PROPERTIES

Character of the Mineral

BAUXITE is a rock, not a mineral species, the predominating constituent of which is free alumina. As mentioned on page 13 it may be of cellular or vermicular structure or it may be like clay or shale or more granular, and frequently it is pisolitic. Microscopic examination does little to elucidate the nature of the rock because of the extremely fine degree of its crystallisation and because of the similarity of the optical properties of the different constituents. Macroscopically it appears to be amorphous but gibbsite may be detected in most bauxites when examined microscopically in thin section, especially in the matrix of a pisolitic or oolitic ore.

Diaspore, when it occurs in crystalline form, consists of flattened prisms or thin scales but in the commercial deposits it is earthy, granular and sometimes oolitic, and it may be grey, brown or red in colour.

Physical Properties

Most of the physical properties of *bauxite* vary widely. The *hardness* ranges from 2 to 7 on the Mohr scale. It is generally greater the less the water content but ores of identical composition may have very different degrees of hardness. The *specific gravity* is also variable, but pure bauxites generally range from 2·5 to 2·6. With decreasing water and increasing ferric oxide the specific gravity generally increases. The *refractive index* has been given as 1·57. The *streak* is variable, *lustre* dull and the *cleavage* irregular. The *melting-point* depends upon the amount of impurity, especially ferric oxide. An upper limit for the pure ore is about 2000°, and the range 1565° to 1785° has been observed [25] on bauxite bricks.

Diaspore has a *hardness* of about 7 and a *specific gravity* 3·4. Its *refractive index* has been given as 1·73, and its *specific heat* as $= 0{\cdot}2085 + 0{\cdot}000127t$.[7]

Gibbsite is comparatively rare but the artificially prepared crystalline hydroxide is of the same form. Its *specific gravity* is 2·4 and its *hardness* 2 to 3.

The physical properties of the important constituent of bauxite, *alumina* (Al_2O_3), are as follows: *X-ray structure*, rhombohedral lattice, hexagonal axis 4·86 Å, vertical axis 6·62 Å.[1] *Specific gravity* of precipitated alumina heated to 600° : 2·28, 700° : 2·83, 800° : 3·39, 900° : 3·53, 1200° : 3·92.[2] Several observers give 3·99 for the crystalline oxide. *Specific heat*, 0·180 at 15°[19], 0·20 at 15°–100°, 0·24 at 15°–420°.[3] The most reliable of a number of *melting-point* determinations give about 2050°. The *vapour pressure* has been given as 7 mms. at 1830°, 108 mms. at 1930°, 300 mms. at 2070° and 750 mms. at 2125°.[4] *Heat of formation*, 387,000 cals.[5] *Index of refraction* (crystalline Al_2O_3) 1·76.

Rankin and Merwin [24] found another crystalline form of alumina (β–Al_2O_3, corundum being α–Al_2O_3) in charges of molten alumina which were slowly cooled. A trace of magnesia assists formation. Apparently it does not revert to the α–form.

Wohlin [16] on heating alumina observed an exothermic change at 1070°, the specific gravity at the same time changing from 3·07 to 3·70, and Houldsworth and Cobb [23] confirmed this on alumina obtained by calcining the nitrate, but observed no such effect on precipitated alumina. Similar exothermic effects were noticed on ferruginous bauxite between 1000° and 1070° and on siliceous bauxite between 940° and 965°. This heat evolution would seem to be due to polymerisation.

Alumina may be obtained as a hydrogel which dries to a horny mass which the X-radiogram shows to be amorphous.[6]

Chemical Properties

The chemical properties of bauxite are those of its important constituent, hydrated alumina, modified by the

presence of impurities, especially ferric oxide and silica. The alumina is soluble in solutions of sodium and potassium hydroxides and in acids, the proportion of the total alumina that is soluble varying with the proportion of impurities and the degree in which they are combined with the alumina. Removal of the combined water decreases the solubility of the alumina and after heating to a sufficiently high temperature the dehydrated ore is chemically very inert. Indeed, fused alumina is used as a packing material in Glover towers. Diaspore, for some obscure reason, is not readily soluble in alkalies.

The behaviour of solutions of alumina in alkali hydroxide solutions has given rise to some doubt as to whether they are true solutions, and Mahin, Ingraham and Stewart [8] suggested that the alumina is merely dispersed in the alkali, but their conclusions have been criticised by Blum [9] who obtained evidence of the formation of definite aluminates and who also pointed out that a crystalline potassium aluminate has been obtained.[10] The solubility of alumina in caustic soda depends on the concentration of the latter. On diluting a saturated strong solution alumina is not at first precipitated, but if freshly precipitated crystalline hydrated alumina is added the excess is gradually thrown down, but not rapidly like crystals from a super-saturated solution. This process, which is the basis of the Bayer method for the production of pure alumina, has been much investigated. Russ,[11] like Bayer and Ditte, assumed that there are two forms of hydrated alumina, gelatinous α and crystalline β. Transformation from α to β is slow, and when the dilution of the strong aluminate liquor causes the formation of hydrated alumina by hydrolysis the α-form is first produced and remains in colloidal solution until transformed into the crystalline β hydrate. Russ measured the solubility of the β-form and found a rapid increase in solutions of caustic soda above 5·2 mols. per 100 mols. water.

Combined Water

The combined water in bauxite, that is the water not removed by drying at about 105°, may be in a state of combination with the alumina to form definite hydrates such as gibbsite and diaspore or it may be in the less definite form of combination of water associated with a colloidal hydrogel. Water of hydration is characterised by being evolved at definite temperatures and with definite heat absorption, but the water of a hydrogel is evolved over a range of temperature with no endothermic arrest points in the heating curve. Haber [6] has shown by the X-ray method that alumina gel may be obtained amorphous and Willstätter and Kraut,[12] Bohm [13] and Guichard [14] have obtained both amorphous and crystalline forms by different methods of preparation. Carnelly and Walker [15] long ago showed that there were arrest points in the heating curve of the precipitated trihydrate. It would therefore seem possible that bauxite might consist wholly of crystalline definite hydrates, wholly of a hydrogel or it might be a mixture, and the experimental work on the different bauxites favours the supposition that they are generally mixtures.

Wohlin [16] found that bauxites of so low a water content that they must be monohydrates show a heat absorption at 540°, whilst more highly hydrated ores have an arrest point at 310°. Kirnakov and Urazov [17] found similar arrest points on Russian bauxites between 202° and 296° and between 509° and 555°. Diaspore showed the higher arrest point, whilst if the silica in the bauxite exceeded about 12 per cent. a kaolin arrest point of 558° to 605° also appeared. Yamaguchi, Takebe and Morioka [18] measured the vapour pressures of diaspore (84 per cent. Al_2O_3, 15 per cent. H_2O) and bauxite (62 per cent. Al_2O_3, 22 per cent. H_2O) by the dynamic method and found the vapour pressure equal to one atmosphere at 502° with diaspore and at the two tem-

peratures 332° and 474° with bauxite. Harrison [20] found an arrest point at about 250° but apparently not at higher temperatures, although the water was not all driven off until a high temperature was attained. Fox,[21] working on Indian bauxite with 26 per cent. water, found that two hours heating at 800° was not sufficient for complete dehydration, about 4 per cent. of the total water content being left in the ore. By gradual heating from 100° he found that about 25 per cent. of the water was evolved between 250° and 270° and most of the remainder between 650° and 750°, very little being lost between 270° and 600°. A temperature over 1000° was required for complete dehydration. Arsandaux [22] obtained rather similar results, and Haber [26] gave 200°, 300° and 420° as the temperatures at which gibbsite, bauxite and diaspore begin to evolve water. Houldsworth and Cobb [23] measuring the loss of weight on very gradual heating (2 to 3 weeks to reach 1000°) found that diaspore lost practically all its water between 370° and 400°, gibbsite lost a large proportion (about 85 per cent.) between 160° and 190° and the remainder very gradually up to 500°, red bauxite (only 12 per cent. H_2O) lost nearly all between 350° and 410° and Irish grey bauxite high in silica (30 per cent.) had losses at 200° to 230° and 400° to 450°. Measuring the thermal effects they found endothermic reactions (arrest points) for diaspore between 470° and 555°, for gibbsite between 240° and 320° and a small effect at 500°, for red bauxite between 490° and 565° and for grey siliceous bauxite between 300° and 365° and between 510° and 610°. All these results are summarised in Table II.

Unfortunately the methods used in most of the investigations were unsatisfactory. Unless heating is carried out in an atmosphere of water vapour the temperature at which decomposition takes place is of little significance, and the " arrest " point is not sharp. Slow heating gives the lowest temperatures. The measurement of vapour pressure should

TABLE II

Observer	Method	Substance	1	3
16	Heating Curve .	Bauxite	310°	540°
17	Heating Curve .	Diaspore Bauxite	— 202°–296°	509°–555° 509°–555°
18	Vapour Pressure . (Dynamic method)	Diaspore (15%) Bauxite (22%)	— 332°	502° 474°
20	Heating Curve .	Bauxite	250°	—
21	Heating Curve .	Bauxite	250°–270°	650°–750°
23	Loss of Weight . Heating Curve .	Diaspore ,,	— —	370°–400° 470°–555°
	Loss of Weight . Heating Curve .	Gibbsite ,,	160°–190° 240°–320°	— 500° *
	Loss of Weight . Heating Curve .	Bauxite (12%) ,,	— —	350°–410° 490°–565°
	Loss of Weight . Heating Curve .	Bauxite (23%) ,,	200°–230° 300°–365°	400°–450° 510°–610°

The figures in parentheses are percentages of combined water.
* There was only a very slight endothermic arrest at 500°.

accurately give the temperature at which the dissociation pressure equals one atmosphere and the results of the one observer using this method are the most valuable. It is desirable that they should be confirmed and supplemented. The bauxite used was so low in water that the trihydrate decomposition temperature of 332° is of doubtful accuracy. It may be too high. The monohydrate (diaspore) figure of 502° should be correct, although it is rather lower than would be expected from the other determinations, and the difference between it and the bauxite figure of 474° is probably to be attributed to colloidal hydrate in the latter.

The conclusions from all these investigations are :

(1) There is definitely no crystalline dihydrate in any of

the samples tested and the existence of any such crystalline form (the " mineral " bauxite, $Al_2O_3.2H_2O$) may be considered finally disproved.

(2) Bauxites normally contain gibbsite ($Al_2O_3.3H_2O$), the dissociation temperature of which is about 300° or a little higher, diaspore ($Al_2O_3.H_2O$), the dissociation temperature of which is about 500°, and hydrated alumina in gel form which evolves its water at all temperatures and does not part with the last trace of it until a very high temperature (about 1000°) is reached.

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CHAPTER VII

THE USES OF BAUXITE

Uses and their Relative Importance

BAUXITE is the ore used in the production of all the metallic aluminium at present made (with the possible exception of a small amount produced in Italy and Scandinavia, see p. 126) and for many years the aluminium reduction companies have been easily the most important bauxite consumers. The other important uses are in aluminous cements, for sulphate of aluminium, in alumina refractories and abrasives and in oil refining, whilst minor uses include the manufacture of other compounds of aluminium and its use in some countries for building and similar purposes, but all these other industries together do not at present require as large a tonnage as the metal industry.

The chemical use of bauxite for producing aluminium sulphate has long been next in importance to its use for the metal, but although statistics are not available it is fairly certain that aluminous cement now employs a larger quantity of the ore than that used for sulphate. In 1926 the bauxite used for aluminous cement in Europe and America together probably exceeded 200,000 tons, and it is increasing rapidly. If bauxite were available at a low enough price it is probable that the cement industry would soon absorb a larger tonnage than the metal industry.

Abrasive manufacture probably ranks next in importance, followed by alumina refractories which are coming more and more into use, the only limitation on their more general use being their high price. Both these applications of the ore are growing steadily. Oil refining does not account for a very large tonnage, but with more knowledge of the reactions involved it may increase in importance. The other uses are not likely to account for an important amount as far as present indications reveal, and the employment of so valuable a material as a building stone,[1] for road making

(e.g. in parts of Australia) or for admixing with mortar to give durability [2] is unlikely to continue.

Statistics

The world's production of bauxite from 1914 to 1926, as far as the information is available,[3] was as shown in Table III.

TABLE III

WORLD'S PRODUCTION OF BAUXITE IN THOUSANDS OF LONG TONS

Year	1914	1915	1916	1917	1918	1919	1920	1921	1922	1923	1924	1925	1926
Austria	—	—	141	163	165	—	—	—	—	—	3	4	5
British Guiana	nil	nil	nil	3	4	2	32	*	*	136	185	194	219
Dutch Guiana	nil	nil	nil	nil	nil	nil	nil	nil	19	16	59	85	48
France	—	—	106	121	145	159	267	95	236	314	382	400	402
Germany	—	—	—	11	14	9	13	10	15	7	3	2	—
G.B. and Ireland	8	12	10	15	10	9	11	2	6	4	5	5	—
India	1	1	1	1	1	2	6	7	5	7	23	10	5
Italy	4	6	8	8	8	3	13	49	67	98	139	192	89
Jugo-Slavia	—	—	—	—	—	—	28	10	31	33	30	78	120
U.S.A.	219	297	432	578	615	383	530	142	315	531	348	317	392
Rumania	—	—	—	—	—	—	—	—	4	4	—	—	1
WORLD	—	—	691	928	963	569	901	318	701	1151	1180	1290	1290

* Mines shut down 1921–2. 20,000 tons shipped from stock 1921.

The bauxite used in the various industries is not known owing to lack of the necessary statistics. Even in America statistics are limited to domestic bauxite which is divided into that used for manufacture of the metal, for chemical purposes and for manufacture of abrasives and refractories. The figures from 1921 to 1926 are as shown in Table IV.[4]

TABLE IV

USES OF BAUXITE IN U.S.A.—THOUSANDS OF LONG TONS

Year	1921	1922	1923	1924	1925	1926
Aluminium	92	212	381	226	173	242
Chemical	41	79	69	55	67	78
Abrasives and Refractories	7	20	73	67	74	72

These figures do not include the large imports of ore from Guiana and from Jugo-Slavia, the former being used almost exclusively for aluminium production and the latter for aluminous cement. Nearly all the bauxite from the Guianas goes to aluminium producers in the United States and Canada. The imports from Jugo-Slavia are said to have amounted to over 100,000 tons in 1926, most of which was employed in making aluminous cement.

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CHAPTER VIII

THE MANUFACTURE OF ALUMINIUM

Preparation of the Ore and Type Required

ALUMINIUM is produced by electrolysing alumina dissolved in a bath of molten cryolite. A commercial process for refining the metal from its important impurities has not yet been evolved and it must therefore be made of the necessary purity in the first instance, by using pure alumina as raw material. The extraction of pure alumina from bauxite is carried out almost entirely by the Bayer process, but to a limited extent also by the Deville-Pechiney and also, quite recently, apparently by the Haglund and Pedersen processes.

The bauxite used must be low in silica and high in alumina. The limits of the impurities allowed vary in different countries but in general the silica should not exceed 5 per cent. and frequently a lower limit than this is demanded, whilst iron oxide and titanium oxide together generally total less than 10 per cent. This latter limit, however, may be and often is exceeded without causing as much trouble as a high silica content (see also p. 34). It is also necessary that the alumina should readily dissolve in solutions of sodium hydroxide of the concentration used in the Bayer process and a test of this solubility is necessary.

The ore reaches the consumer either in its natural state or after partial drying, and generally it is of varying size. It is dried if necessary and sometimes calcined at low temperature to remove organic matter and is then ground to a fineness of nearly all passing 100 mesh or sometimes finer, after which it is ready for the chemical process of alumina extraction.

Bayer Process

The Bayer process depends upon the reactions :

$$Al_2O_3 + 6NaOH = 2Na_3AlO_3 + 3H_2O$$

and $$Na_3AlO_3 + 3H_2O = Al(OH)_3 + 3NaOH$$

or $$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O$$

and $$NaAlO_2 + 2H_2O = Al(OH)_3 + NaOH$$

The actual quantities reacting represent something between the two, but closer to the second equations. The formation of sodium aluminate is carried out by digesting the powdered bauxite with soda solution of specific gravity about 1·45. The powder is thoroughly stirred with the solution in a mixer and the mixture run or pumped into steam-jacketed autoclaves where it is kept agitated and where it remains for between 3 and 8 hours, according to the nature and fineness of the ore, at a pressure of from 50 to 70 lbs. per square inch (corresponding to a temperature of about 160°). The alumina dissolves, the impurities ferric oxide and titania remain undissolved whilst the silica is partly dissolved as sodium silicate and partly unaffected. The part that dissolves further reacts to form a double salt : $Na_2O.Al_2O_3.SiO_2.9H_2O$, which is insoluble (the formula generally ascribed to the double salt is as given, but there is some doubt about it and the authorities differ. Pukall [1] found the compound $2SiO_2.Al_2O_3.Na_2O.2H_2O$ to be formed under rather similar conditions). There is therefore little silica left in solution but each unit weight of silica results in the loss of 1·7 parts of alumina and 1·3 parts of caustic soda and it is important to minimise this loss by using a low silica ore. The loss is reduced by adding lime to the bauxite (generally during grinding) which combines with the silica to form calcium silicate which is insoluble, but lime also combines with alumina so that the addition must be carefully regulated, and it is not an effective expedient if the silica in the bauxite is high. In general about 90 per cent. of the alumina in the ore is obtained in solution, the

remainder being left in the undissolved sludge either as a residue or as a precipitate of the double salt mentioned above. According to Neumann and Reinsch [2] pressure is not necessary in the solution of the bauxite. They say that the same results are obtained by using a more concentrated solution of soda boiling at 160°, but it would seem that their proposed method is not in actual use anywhere.

The liquor from the digestors passes into large iron settling tanks where it remains several hours and where the bulk of the undissolved sediment (red mud) settles out. It is then diluted to specific gravity 1·23 with washings from previous cycles and run through filter presses to remove the last traces of red mud, the filtrate passing into large precipitation tanks fitted with agitators. Freshly precipitated hydrated alumina is added in small quantity to start precipitation and in these tanks the reaction represented by the second and fourth of the equations on page 54 takes place. Precipitation occupies 48 hours or longer. The silica in solution does not precipitate to any considerable extent until nearly all the alumina is removed, and by retaining some alumina in solution a nearly silica-free precipitate is obtained. Precipitation is generally arrested when the alumina : soda ratio in solution reaches 1 : 6.

The liquor with its precipitate in suspension is passed through filter presses, the filtrate, containing all the soda, some alumina and a little silica, being evaporated for use again in the digestion process. The alumina, which filters readily if properly prepared, is washed and drained, and the washings from the filter presses are used for the dilution of the sodium aluminate liquor. The red mud is washed to recover soda and the washings used for dilution or evaporated to produce concentrated liquor for digestion.

The process as outlined above is subject to minor modifications embodying modern improvements such as continuous vacuum filters, counter-current washing in thickeners, etc.

Deville-Pechiney Process

This process, also called the " Le Chatelier-Morin," the " Carbonate " or the " Dry " process, was formerly the principal one used and it is still employed to a very limited extent for bauxites high in iron and low in silica. The ground ore is mixed with a weight of anhydrous sodium carbonate equivalent to about 1·5 mols. carbonate to 1 mol. alumina and with an allowance for silica, iron oxide and titania, and generally a little powdered coal is added. The mix is roasted in a reverberatory or rotary furnace at 1000° to 1200°, special care being taken to avoid actual fusion. The reactions are :

$$Al_2O_3 + 3Na_2CO_3 = 2Na_3AlO_3 + 3CO_2$$

and $$Al_2O_3 + Na_2CO_3 = 2NaAlO_2 + CO_2$$

The dirty green crumbly mass is ground and lixiviated with boiling water or with hot weak liquors from previous extractions, when the aluminate goes into solution together with any silica (as sodium silicate), whilst the iron oxide and titania remain undissolved or are precipitated and are settled out. Care must be taken to avoid absorption of carbon dioxide from the air during extraction. The liquor is filtered and treated at about 60° with waste gases containing carbon dioxide which precipitates the alumina in accordance with the equations :

$$2Na_3AlO_3 + 3CO_2 + 3H_2O = 2Al(OH)_3 + 3Na_2CO_3$$

and $$2NaAlO_2 + CO_2 + 3H_2O = 2Al(OH)_3 + Na_2CO_3$$

The alumina is filtered off and washed, the sodium carbonate solution evaporated, and the dry carbonate used again.

There is generally enough silica in solution seriously to contaminate the alumina. To remove it the liquor before treatment with carbon dioxide may be heated in an autoclave to about 85 lbs., when the insoluble silico-aluminate is formed, which may be filtered off. Alternatively a nearly silica-free alumina may be produced by arresting the precipitation process before all the alumina is removed.

Peniakoff Process

In this process the powdered bauxite is mixed with sodium sulphate and coal and the mix heated in a rotary furnace at 1200° to 1400° :

$$Al_2O_3 + 3Na_2SO_4 + 3C = 2Na_3AlO_3 + 3CO + 3SO_2$$

The sulphur dioxide is used to produce sodium sulphate from common salt by the Hargreaves process :

$$2NaCl + SO_2 + O + H_2O = Na_2SO_4 + 2HCl$$

hydrochoric acid being a by-product. The alumina is precipitated with carbon dioxide or as in the Bayer process. The process might be used to make up for losses of soda in the Bayer process, but it does not appear to have been a commercial success although tried out on a large scale.

Haglund Process

This process [3] eliminates the usual impurities of bauxite by reducing them to the elements. Many proposals have been made to reduce the ferric oxide and silica by fluxing in an electric furnace with carbon, but the practical difficulties seem to have first been solved by Haglund who adds 25 per cent. of aluminium sulphide to the charge. This sulphide may be produced separately by fusing together bauxite, coke and sulphide of iron, or it may be formed in the main reaction by the addition of iron sulphide to the charge. Fluxed with the alumina it produces a very fluid slag of comparatively low melting-point. The products of reaction are ferro-silicon, a valuable by-product, and alumina-aluminium sulphide slag, which on cooling separates into crystalline alumina and sulphide. The mass is crushed and treated with water, when the sulphide is decomposed to hydrated alumina and hydrogen sulphide. The alumina is purified by classification, etc., and is said to contain less silica than Bayer alumina but rather more iron. It is also

said that anhydrous aluminium chloride can be produced directly from the sulphide by reacting on it with hydrogen chloride. The hydrogen sulphide produced by hydrolysis may be used for sulphurising the bauxite during its calcination, with resulting saving in the sulphide required for fluxing.

It is said that the Haglund process is being used commercially for the production of alumina for aluminium manufacture but it is not easy to see how a product sufficiently low in iron can be made. Extensive use of the process would result in an over-production of ferrosilicon and reduce the return from this by-product, but there is room for wide expansion, before such over production is felt.

Serpek Process

The Serpek is primarily a process [4] for the fixation of atmospheric nitrogen but it provides pure alumina as a by-product and it seems probable that it will prove valuable in the future when operated in conjunction with aluminium manufacture. It is based on the observation that aluminium nitride is formed when nitrogen is passed over a mixture of alumina or bauxite and carbon heated to 1600° or more. Various catalysts promote the reaction.

$$Al_2O_3 + 3C + 2N = 2AlN + 3CO - 213{,}000 \text{ cals.}$$

Although an experimental plant has been erected the process has not yet been perfected, difficulties being encountered in providing a structure that will withstand the drastic temperature conditions and at the same time provide for the simultaneous absorption of nitrogen and evolution of carbon monoxide. The latest type of furnace is a rotary cylinder with a peculiar form of internal electrical heating, the charge of bauxite and carbon forming the resistance.

The nitride formed according to the above equation is boiled under pressure with water, when it is hydrolysed

with liberation of ammonia and production of hydrated alumina:

$$AlN + 3H_2O = NH_3 + Al(OH)_3$$

Combining the Serpek with the Bayer process the nitride is boiled at about 30 lbs. pressure with soda from previous alumina precipitations. Sodium aluminate is formed and ammonia evolved. The aluminate is diluted and precipitated as in the ordinary Bayer process.

Pedersen Process

At first sight this process [26] seems to have little to recommend it, but it is said to be in use in Norway so apparently is commercially successful. Bauxite, which may be very ferruginous, is smelted to produce low sulphur iron and a calcium aluminate slag. Iron ore may be added if the bauxite is not sufficiently high in iron. The slag is leached with a hot solution of sodium carbonate containing also free caustic soda and sodium aluminate is formed in solution. The alumina is precipitated partly by the Bayer method and partly by carbon dioxide so that finally a dilute solution of sodium carbonate and hydroxide remains ready after concentration for the treatment of more slag. The process would seem to be useful for treating high iron bauxites but it is not clear what limits of silica are allowable. Presumably the leaching of the slag must be carefully controlled if solution of silica is to be avoided.

Treatment of the Hydrate of Alumina

The hydrate of alumina produced by any of the above processes must be dried and dehydrated to produce anhydrous alumina for use in the reduction process. Dehydration is carried out in short rotary kilns fired by producer gas, the temperature used being 1000° to 1100° at the hot end of the kiln, and the combined water is reduced

to 0·5 per cent. or less. The alumina is cooled in a rotary cooler. The main difficulty in the calcination process is in preventing loss of dust. The partially calcined alumina is very " lively " and inclined to dust and also to run through the kiln, but after a certain stage it becomes " dead " and sandy. A small quantity of calcium fluoride (less than 1 per cent.) is often added to the alumina to reduce the temperature at which this change occurs. Dust catchers, generally in the form of large settling chambers, are built to recover alumina dust from the kiln exhaust gases.

The alumina produced is of a high degree of purity, the silica content generally being less than 0·1 per cent. and the ferric oxide very much lower. There is more soda present than any other impurity, the Na_2O content sometimes reaching as high as 0·5 per cent.

By-Products

The red mud from the Bayer process contains practically all the impurities in the bauxite used and its composition therefore varies with that of the bauxite. The following analysis has been given as typical : [5] Al_2O_3 7·0 per cent., Fe_2O_3 37·6 per cent., SiO_2 3·5 per cent., TiO_2 4·6 per cent., Na_2O 3·7 per cent., Combined water 4·2 per cent., Free water 39·4 per cent. Many bauxites contain much more titanium than this analysis indicates, and some Indian ores would give as much titanium oxide as iron oxide.

The red mud has been used as a cheap pigment, especially for colouring cement, for towns gas purification, and to a very limited extent, after cintering, as an ore for iron. Some bauxites are highly coloured and there is also a fair range of colours from light red to purple, and by a more careful study of the problem the use of the mud for pigment production could be extended. At present the mud from the majority of alumina works is a waste material. By fusion with sodium carbonate more alumina may be

obtained suitable for conversion into the sulphate and the residue is better than the original mud as a pigment and is also suitable as a polishing medium.[6]

The titanium dioxide in the bauxite remains in the red mud and as the highly titaniferous bauxites of India and elsewhere come into use this source of titanium will become more and more important. A cheap method of separating the titanium dioxide from the ferric oxide and other impurities would provide a supply of the former for use as a white pigment in paints and for other purposes.[27] Its valuable properties in this direction are already well known and it commands a high price in the pigment market. It seems certain that such a process will soon be worked out and that the red mud will become a very valuable by-product of alumina manufacture. At the same time the market value of the Indian and other titaniferous bauxites will be enhanced. The process of Dutt [7] may be applicable.

The Reduction Process

The electrical process of aluminium production at present used is called the Hall-Héroult after the simultaneous patentees in America and Europe respectively. Nevertheless the Hall patents were preceded and dominated by patents taken out in America by Bradley. The process consists in the electrolysis of alumina dissolved in a bath of molten cryolite containing certain other compounds to lower the fusion temperature. The cathode of the bath consists of the molten aluminium which collects on the bottom. The mixture used in the bath must therefore be of lower specific gravity when molten than molten aluminium. It must melt at moderate temperatures—not above 900° and preferably at about 800°—for reasons to be given later, and at this temperature it must dissolve about 20 per cent. of alumina to furnish a rich enough solution for electrolysis. It must not be decomposed by the current more readily than

alumina, nor must it react with the aluminium formed and it must not be liable to decompose producing compounds of higher melting-point which would solidify and clog the bath. Finally its price must be reasonable and its conductivity high.

Cryolite, $3NaF.AlF_3$, melts at about 1000° and although its melting-point is reduced by the addition of alumina until the eutectic is reached, probably with about 15 per cent. alumina at 935°, further addition of alumina raises the melting-point and in practice it is necessary to add another flux to lower it sufficiently. Moreover the specific gravity of a saturated cryolite solution is higher than that of molten aluminium. Sodium, calcium and aluminium fluorides are effective as fluxes and they also reduce specific gravity. The properties of mixtures of these compounds have been carefully investigated,[8] but the exact composition of the electrolyte used is kept a secret. Some combination of the above compounds is always employed.

Furnaces, baths, cells or " pots " of various sizes and shapes are used. In general they are rectangular and an average is, perhaps, 8 ft. × 5 ft. × $2\frac{1}{2}$ ft. high outside dimensions, although much larger units than this are now in use. They consist of a steel casing lined with a mass of compressed carbon (ground coke bonded with pitch) which may be up to 12 inches thick on the sides and thicker on the bottom. In the bottom of the cell are set a number of blocks of high conductivity carbon in good electrical contact with the steel sides or otherwise electrically connected with the negative pole of the electrical supply. The whole of the lining thus forms the cathode but as the electrolyte tends to solidify on the sides the cathode area is limited to the bottom. As the metal collects here the effective cathode surface is the aluminium. The bottom is generally slightly sloped to a tapping hole on one side.

The anodes are carbon blocks square in cross section varying from 8 inches to 16 inches square and anything up

to 3 feet long. They are suspended from above close together in groups of 8 to 12 to each cell. Electrical connection is made by aluminium, iron or copper bars screwed or burnt into the carbon blocks.

The anodes, which are gradually burnt by the oxygen liberated, are an important item of cost, anode consumption varying from 0·6 to 0·8 lb. per lb. metal. They must be very low in ash because this passes into the electrolyte and contaminates the metal. Petroleum coke is used. It is broken to nut size, heated in retorts or vertical electric calciners to red heat to remove the bulk of the 15 per cent. volatile matter that it generally contains, ground finely in ball mills, mixed with tar or oil as a binder and moulded into blocks under high pressure. The blocks are baked in a furnace to a final temperature of 1300° to 1400°, heating being very gradual to avoid cracking, and a tunnel kiln is sometimes used, the anodes being stacked on the trucks and covered with loose carbon, etc. In one form of furnace the anodes stacked in steel baskets and packed around with coke are heated by passing a heavy current through them. The baking process generally lasts 6 days or longer, but according to Schuchardt [9] they can be made of as good quality with short baking at a higher temperature.

The anodes dip into the molten electrolyte to within about 2 inches of the surface of the molten aluminium. In operation the surface of the electrolyte is solid and the alumina added is placed on this surface and left there until the voltage drop across the cell indicates the need for a further supply, when it is stirred into the molten electrolyte. Unless the voltage is allowed to become too high the cryolite itself should not decompose, but there is always some loss of fluorine, which is made up by the addition of aluminium fluoride.

The decomposition voltage of alumina has been given as about 2·2 volts [10] but the actual cell voltage generally lies between 6 and 7·5 volts. The current efficiency depends

very largely on the temperature of the electrolyte, because the main loss of efficiency is due to metal fog formation—an important source of loss in all molten electrolytes—which increases rapidly with increase of temperature, hence the need for a cryolite mixture of low melting-point. Technical cells operate at about 900° and the efficiency generally lies between 70 per cent. and 80 per cent. At 7 volts and 75 per cent. current efficiency it takes 12·6 K.W.H. to produce 1 lb. of aluminium. The anodic current density used ranges from about 0·6 to 2·0 amps. per sq. cm. but it is generally considered that it should not exceed 1·0.

The specific conductivity of the electrolyte in a technical cell is about 2 reciprocal ohms per cubic centimetre. It increases with increasing concentration of alumina in the solution.[11] Nevertheless, as the alumina becomes exhausted in a cell in operation the voltage rises, and it is this rise of potential—the " anode effect "—that is used as a guide to the alumina requirements of the cells. The anode effect is due to a rise of potential difference at the anodes owing to too low an alumina concentration and to the fact that the decomposition voltages of the fluorides are very much higher than that of alumina. The rise of voltage is sharp and it is accompanied by arcing at the anodes. It has been the subject of much investigation.[12]

Aluminium cells are generally arranged 20 to 40 in series and currents of from 8000 to 15,000 amperes are common whilst 20,000 ampere units are now used. The output of each cell may be from 7 to 14 cwt. of metal a week, this amount being tapped off in two portions, that is bi-weekly, or sometimes more often.

Cryolite and its Preparation

The consumption of cryolite in aluminium production is generally placed at about 0·1 lb. per lb. metal. It is a rare mineral, the only workable deposit known being at Ivigtut in

Greenland, whence a considerable portion of the total supply is obtained.[13] It is also made synthetically from the much cheaper and more widely distributed fluorspar (CaF_2) by distilling off the hydrofluoric acid with sulphuric acid and neutralising with alumina and soda in the right proportions. Aluminium fluoride is similarly prepared. In another process[14] fluorspar is heated with potassium sulphate and carbon:

$$CaF_2 + K_2SO_4 + 4C = CaS + 2KF + 4CO.$$

The readily soluble potassium fluoride is extracted with water, sodium sulphate added and slightly soluble sodium fluoride separated. Cryolite is formed by adding aluminium sulphate to the sodium fluoride solution.

Other Processes of Aluminium Production

Suggestions have frequently been made for the direct smelting of bauxite in a blast furnace. Alumina can be reduced by a purely thermal process, but the temperature at which the reaction takes place is above the boiling-point of the metal, so that it would be volatilised in a blast furnace and carried forward with the gases, to be reoxidised higher up in the furnace. Furthermore, the problem is complicated by the fact that aluminium reacts with carbon monoxide and with carbon. By diluting and removing the carbon monoxide and working under high pressure to reduce vaporisation of aluminium Hutton and Petavel[15] prepared about 50 grams of the metal, and others have made mixtures of aluminium and its carbide, but the experiments are of theoretical interest only.

It has been proposed to electrolyse aluminium sulphide instead of the oxide, the advantages claimed being the relatively low anode consumption, a lower decomposition voltage and the availability of the sulphur for use again after condensation. The sulphide is produced by heating together in the electric furnace bauxite, carbon and a sulphur compound.[16]

Various claims have been made to have deposited the metal from aqueous solution and many patents have been obtained for alleged processes, but they are all doubtful. It has, however, been deposited from a solution of the bromide in ethyl bromide by Plotnikoff [17] and by Patten.[18] It has also been proposed to electrolyse aluminium sulphate in oleum solution.[19]

Aluminium Refining

Many attempts have been made to carry out with aluminium a process analogous to that of electrolytic copper refining. If such a process were available and not too costly it would enable the aluminium producer to employ less pure materials in the process of manufacture and this, in turn, would widen the choice of raw materials. Hoopes [20] and Betts [21] over 20 years ago proposed alloying the metal with a heavy metal such as copper and using an electrolyte heavier than cryolite so that the pure aluminium would float on it, and Tucker [22] proposed a cryolite bath with both anode and cathode on the bottom separated by an insulating wall. The practical difficulties were not overcome until the recent introduction of the new Hoopes cell which is divided horizontally by a water-cooled joint. The lower half, lined with carbon, contains the anode metal, a copper-aluminium alloy, and the electrolyte is cryolite with added aluminium and barium fluorides and saturated with alumina. Graphite electrodes dip into the aluminium cathode which floats on the electrolyte and which is protected from oxidation by a frozen crust of the latter. The working temperature is said to be between 900° and 1100° and the voltage 5 to 7, whilst the current efficiency is said to be high. Metal of purity 99·8 per cent. is regularly produced and much purer samples, up to 99·98 per cent., have been made,[23] the ordinary metal generally being between 98 per cent. and 99 per cent. pure. Unfortunately, although the anode metal may be high in silicon it must be low in iron and titanium

otherwise its melting point will be too high, and this limits the commercial value of the process.

The properties of the pure metal made by this refining process have been investigated by Edwards [24] and Guillet [25] and although it seems much less susceptible to corrosion than ordinary aluminium its mechanical and electrical properties are not very different. Under ordinary atmospheric conditions it retains a brighter surface than the ordinary metal and probably it will find application for ornaments, household utensils, etc., and for chemical apparatus. Articles are now produced consisting of ordinary aluminium with a surface coating of the refined metal. They are sold under the name of " Alclad."

Uses of Aluminium

The uses of aluminium have grown enormously in volume and number in recent years, and in quantity produced it now ranks fourth of the non-ferrous metals, whilst the rate at which its production is increasing makes it certain that it will rapidly move to a higher position. Its outstanding advantages are its lightness, resistance to atmospheric and other corrosion, and its high thermal and electrical conductivity, whilst certain of its alloys are notable for their high tensile strengths. Aluminium castings are used in railroad car, motor car and especially airship and aeroplane construction, in the construction of innumerable fittings for houses, shops, etc., and in electrical work. The sheet metal is employed for cooking vessels and other domestic uses and in the production of toys and all sorts of light articles. The wire is being employed more and more extensively for electric transmission lines and for other purposes, and aluminium powder is used for the thermite welding process, for aluminium paint, in explosives (ammonal) and for " calorising " metals. A special form of flake aluminium made by stamping the sheet metal into

tiny thin flakes is used for paint. A rapidly expanding outlet for aluminium is the chemical industry where it is excellent for organic and many inorganic acids, for fine chemicals and food-stuffs. Besides being highly resistant to corrosion except by alkalies its products of corrosion are colourless and non-poisonous. It is highly resistant to sulphuric and nitric acids and the latter acid is now transported from Norway and Sweden in aluminium containers. Apparently it is not suitable for nitric acid made from sodium nitrate because of the chlorine compounds that occur in that acid.

Aluminium forms a large number of useful alloys which have been and still are being carefully studied. Magnalium (aluminium-magnesium) and Duralumin (aluminium-copper-manganese-magnesium) have been much used for airship construction on account of their combination of strength with lightness, and Alpax and other aluminium-silicon alloys are becoming popular in the foundry. There are several excellent treatises on the aluminium alloys.

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The latter three books deal particularly with the properties of the metal and its alloys.

CHAPTER IX

ALUMINOUS CEMENT

Introductory

ALUMINOUS cement may be defined as a calcareous hydraulic cement containing relatively little silica and a high percentage (say over 30 per cent.) of alumina. It is prepared by fusing or cintering together bauxite and lime.

Aluminous cement is a fairly recent discovery. Although Roth [1] as long ago as 1883 proposed the use of bauxite in cement manufacture he did not contemplate making a true aluminous cement. Its discovery by Bied seems to have been made [2] in an attempt to produce a cement which would be unattacked by sea water. Vicat had stated that if the ratio $(SiO_2 + Al_2O_3) : (CaO + MgO)$ was greater than unity the cement would be unattacked. Increase in the silica content would produce a metallurgical slag of little cementing value so Bied tried increasing the alumina with the ultimate result of producing an entirely new cement. He took out patents in France in 1908 and at the same time Spackman and Lazell [3] in America patented a similar composition and later manufactured and sold it under the name of " Alca," but as an accelerator for lime plaster, etc.: not as a cement. Although " Alca " was apparently made by fusion of the raw materials it would seem that Spackman had no conception of aluminous cement as it is known to-day. He said [4] that the " Alca " had practically the same value in admixtures whatever its composition between the limits of the compositions of the known compounds of lime and alumina or whether they were fused together or merely heated to drive off the volatiles. In the latter instance there could be no combination of alumina and lime and the alumina must have acted in much the same way as pozzolanic silica. Bauxite has long been used in this way in certain regions.[5] However, the forty-three claims of their 1908 patent and the eighty-three of their 1912 patent seem fully to cover aluminous cement manufacture.

The first published description of aluminous cements was a very short one by Bied [6] in which he noted their most striking properties. He was apparently aware of the essential constituent—monocalcium aluminate—but had an incorrect conception of the nature of the setting process. In 1916 the Bureau of Standards in America produced aluminous cement on a small scale,[7] and at about the same time it was being made on a larger scale in France and was used by the French armies. At the end of the war aluminous cement was placed on the market in France under the name " ciment fondu." It is now being manufactured in England, the United States, Italy, Indo-China and apparently also in Germany, as well as in its original home, France.

In spite of the pioneer work done in France in the manufacture of aluminous cements no information as to their constitution and mode of setting has emanated from that country. Killig [17] in 1913 conducted a series of tests which showed the slow setting, rapid hardening, properties of the " acid " aluminates and Endell [18] in 1919 submitted full details of his work which to some extent defined the range of these cements and demonstrated their valuable properties, but the first complete and systematic work on the conditions to be observed in manufacture and on their setting was published in America by Bates.[8] They have also been examined by Dyckerhoff,[28] Radeff,[29] and Berl and Löblein.[30]

Theoretical

It has been shown [9] that lime and alumina combine to form four distinct compounds : $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $CaO.Al_2O_3$ and $3CaO.5Al_2O_3$. In Portland cement of normal composition the only compound is tricalcium aluminate,[9, 10] which is considered to be responsible for the initial set, but which is thought by some to confer little towards the ultimate strength of the cement. A high

alumina content in Portland cement is undesirable because of the rapid initial set, which makes it inconvenient to use.

Bates [8] prepared the four compounds and investigated their properties. He considered that only the two compounds $CaO.Al_2O_3$ and $3CaO.5Al_2O_3$ promised to be of technical importance as cements and he then prepared mixtures of these two compounds in fair quantity by cintering lime and alumina in a 20 ft. × 2 ft. rotary cement kiln, using in some instances nearly pure lime and alumina and in others adding silica, iron oxide and magnesia as impurities. His work also showed that $5CaO.3Al_2O_3$ sets hard but it is too rapid setting for commercial purposes.

Compared with the compounds in Portland cement the aluminates present in aluminous cement have low melting-points. Rankin [9] has shown that the eutectic of $CaO.Al_2O_3$ and $5CaO.3Al_2O_3$ melts at 1400° and that of $CaO.Al_2O_3$ and $3CaO.5Al_2O_3$ at 1590°, whilst the addition of impurities such as silica and iron oxide, especially the latter, considerably reduce these figures. Aluminous cement as at present made commercially generally fuses at under 1400°. On the other hand the temperature at which cintering (and combination) takes place is little if at all below the corresponding temperatures for Portland cement. In other words aluminous cement has a narrow " firing range " and if it is to be produced by cintering in a rotary kiln the temperature must be very closely controlled to ensure combination on the one hand and prevent fusion on the other.

In his experiments Bates [8] employed burning temperatures from 1460° to 1500° for his pure lime and alumina mixtures and as low as 1360° for mixtures containing large amounts of silica. Unfortunately his mixtures were all much lower in iron oxide than commercial cements and the impure mixtures all had more silica than is now in practice allowed.

The raw materials available for aluminous cement manufacture always contain silica and iron oxide and it is

therefore important to know the effects of these constituents. Regarding silica it has been shown [9] that in addition to the calcium silicates which occur in Portland cement the following compounds are possible: $CaO.Al_2O_3.2SiO_2$, $2CaO.Al_2O_3.SiO_2$ and $3CaO.Al_2O_3.SiO_2$. Bates found both $2CaO.SiO_2$ and $2CaO.Al_2O_3.SiO_2$ in his cements and he could find no setting properties in the latter. It therefore acts as a diluent in the cement, and in addition uses up alumina (170 parts for each 100 parts of silica). The orthosilicate $2CaO.SiO_2$, on the other hand, if present in the α or β forms has a definite value in conferring increasing strength with the ageing of the cement. Bates [8] found that insufficient burning caused dusting of the clinker, due apparently to the presence of the orthosilicate and its reversion to the γ form on cooling, and the same phenomenon has often been experienced in attempting commercial production of these cements. His work rather suggests that a high burning temperature favours the formation of the ternary compound $2CaO.Al_2O_3.SiO_2$, whilst at the same time the orthosilicate does not revert to the γ form. The composition of commercial aluminous cements places them in a region where apparently either compound may be formed, but the presence of iron oxide complicates matters and makes it difficult to predict from the data obtained on the system CaO-Al_2O_3-SiO_2. In spite of this uncertainty it is clear that the silica must be comparatively low to produce a suitable cement commercially. If the silica is high the mixture enters the region where ternary compounds of no cementing value are always formed and therefore where alumina is wasted.[34] In aluminous cement practice the silica is always less than 10 per cent. It is claimed [16] that sulphur or sulphur dioxide lessens the tendency to form silicates without hydraulic properties and by passing SO_2 into the furnace during the production of aluminous cement it is said that a higher silica is permissible or a better cement made.

As far as is known iron oxide acts merely as a diluent in aluminous cement. It is highly probable, if not certain, that its presence modifies the behaviour of the cementitious compounds just as they modify the properties of one another (e.g. tricalcium aluminate behaves very differently in Portland cement where it is intimately associated with orthosilicates, etc., than by itself) but the exact nature of the effect is unknown. All that can be said is that there must not be too much iron oxide present if a good cement is to be made and it generally ranges from 7 per cent. to 12 per cent. calculated as Fe_2O_3. A moderate amount of oxide of iron is desirable in processes in which the cement is completely fused because of its effect in reducing the melting-point of the mix, and it is desirable in the cintering process also on account of its facilitating cintering. It will be seen later that in some processes the excess of iron oxide is eliminated by reduction to metallic iron.

When mixtures of lime and alumina in the proportion necessary for aluminous cement formation are heated, the lime first combines with a portion of the alumina to form compounds higher in lime than those in the final cement. This is because the higher lime compounds have a lower melting-point than the compounds in the final cement. Underburning will therefore result in the presence of free alumina, not of free lime (unless the underburning is excessive) and there is little danger of finding free lime in these cements. In Portland cement, of course, conditions are reversed. The low lime compounds have there the lowest melting-point and the higher the lime content the longer it is necessary to burn and also the higher the required temperature.

Monocalcium aluminate, the 3 : 5 aluminate and the 5 : 3 compound are all hydrated by water with the formation of hydrated tricalcium aluminate and the liberation of alumina (but see p. 88). Since the tricalcic compound itself has little value as a cement it is presumed that the high strength

developed by the aluminous cements is due to the liberation of colloidal alumina. This phase of the problem, however, still requires much elucidation. It has perhaps too hastily been assumed that the behaviour of tricalcium aluminate by itself—it hydrates almost instantaneously and does not set hard—is a guide to its behaviour when associated with other compounds and when hydration takes place slowly.

Processes of Manufacture

Details of the processes used by the manufacturers of aluminous cements are kept secret by them. The original patents have expired, and although many furnaces for the production of these cements have been the subjects of patents in recent years the specifications reveal little of value to actual manufacturers.

" Ciment fondu," the first aluminous cement to be made commercially, was at first largely produced in electric furnaces of the arc type and it is still being made in this way to a limited extent. The original experimental work apparently was carried out in small blast furnaces similar to those used in copper smelting, and this process of manufacture was extended and ultimately came to be used in all the large European plants. It is now being replaced by cheaper methods.

In this type of furnace the raw materials are lump lime (preferably hard burnt), lump bauxite and hard metallurgical coke of low ash content, which are weighed out separately in comparatively small quantities to ensure correct proportioning, mixed and fed in at the top of the furnace in the usual way. Preheated air is blown in at the bottom through tuyeres of the usual design and the fused slag is withdrawn through tapping holes. Tapping is generally continuous and a plate conveyor type of slag cooler is often used to ensure rapid cooling and reduce to a minimum the tendency to " dust." According to Berl and Löblein,[30]

however, slow cooling gives better hydraulic properties. Metallic iron is produced in the furnace and it is often rather difficult to separate it from the slag, and care is necessary to avoid freezing of the iron in the furnace bottom. The furnaces used are small units 3 feet to 4 feet in diameter and 10 feet to 14 feet high with outputs of 20 to 30 tons of cement a day, but there seems to be no reason why much larger units should not be employed. The portion of the furnace where fusion takes place is unlined and water jacketed. The coke consumption is heavy—said to be 8 to 10 cwts. per ton of cement—but so high a fuel consumption must be due to the water cooling, small size of furnaces and absence of regenerative stoves, and it could doubtless be reduced. In such small furnaces it is necessary that the lime be added as burnt lime, not limestone, and it is generally produced in mixed-feed kilns. Lumps of lime and bauxite about 3 inches diameter are preferred. Small bauxite cannot be used and since many ores are rather soft and friable it may be necessary to have a briquetting plant to deal with the smalls made in transit and handling. A small percentage of the finished cement may be used as a binder.

The high consumption and costly nature of the fuel used in this process make it a heavy item in the cost of production. To meet this disability furnaces have now been designed which can be fired with powdered coal.[11] They consist essentially of a reverberatory furnace in conjunction with a vertical recuperator or preheater. The open furnace is fired by powdered coal and it is here that fusion takes place, the hot gases passing on to heat the lump lime and bauxite fed in at the top of the vertical recuperator and which pass down into the molten cement on the hearth of the furnace. Successful operation depends on careful control of rate of feed and heat so that the material is not fused in the vertical shaft but rapidly fused on the hearth, and a point of weakness in the refractory lining of the furnace is the arch at the point where the hearth opens into the shaft. The arch

bricks here have to withstand the fluxing action of free lime at high temperature. When any fusion takes place in the vertical shaft it tends to choke the draught, and to provide for this there is an auxiliary flue leading off the body of the furnace which may be brought into use by opening a damper.

In addition to the merit of permitting the use of cheap fuel this type of furnace has the advantage of allowing a considerable charge of molten cement to be retained in the furnace, thus helping to reduce any inequalities in composition due to uneven feeding of the raw materials or their uneven passage down the furnace. The separation of metallic iron and cement is also facilitated, and the chance of freezing the iron reduced. Unburnt chalk or limestone is now being used instead of lime in these furnaces.

As an improvement on the usual blast furnace method Eckel [12] proposes the use of high furnaces with lines like an ordinary blast furnace for pig iron and with regenerative stoves and gas recovery. As raw material he proposes using limestone, ferruginous bauxite and, generally, iron ore, and tapping is to be discontinuous the better to separate slag and metal. This suggestion, which of course has often been made, has the obvious disadvantage of providing a very large unit and in the proposed process it would be difficult to keep the silica sufficiently low unless very pure iron ore is used. There are, however, aluminous laterites low in silica which could be used in this way for simultaneous iron and cement production, whereas they are too impure for any other use. It seems likely that some day aluminous cement will be made on a large scale from such ores.

Furnaces of the types mentioned have been used exclusively in Europe but the American producing company has followed more closely standard Portland cement practice and the experimental work of the Bureau of Standards. The raw materials, bauxite and limestone, not lime, are finely powdered, intimately mixed and fed to a rotary kiln. It is impracticable to fuse completely in a rotary kiln, so the mix

is cintered, but to ensure complete reaction cintering is carried almost to the point of complete fusion and the clinker produced is more like a slag than a Portland clinker. In this condition the hot clinker does not discharge freely from the kiln and it is understood that special means of removing it are adopted. The discharge arrangements, in fact, seem to be the only marked departure from ordinary cement practice (dry process), but it is necessary to control temperature more closely to ensure a sufficient degree of cintering without complete fusion. The fuel consumption is much the same as in Portland cement production.

The rotary kiln process has important advantages over processes which use lump materials in that it facilitates cheap and easy handling of the raw and cintered materials, permits very close proportioning of the constituents and the use of bauxite of all sizes and of any degree of friability. The overall thermal efficiency, too, should be higher on account of the two operations of lime burning and cement cintering being done in the one furnace, but this is doubtless off-set by the relative inefficiency thermally of the rotary kiln as a furnace. Like the reverberatory furnace process it permits the use of cheap fuel (coal dust) but the necessity of keeping down the silica content limits the choice to rather low ash coals. A disadvantage in many countries, and especially in the present condition of the aluminous cement industry, which is only in the initial stages of its development, is the large size of the ordinary rotary kiln unit coupled with the relative inefficiency of small units.

Aluminous cement, as far as can be seen, will always be a comparatively costly cement, and in judging between the different processes of manufacture the quality of the product is of relatively more importance than economy in costs of manufacture. Independent data sufficient to permit a final judgment between the processes are not yet available, and since improvements are constantly being made it is probably too early to make a choice. The best test results have

been obtained with cement made by complete fusion and it is perhaps significant that the pioneers in aluminous cement making, although they produce Portland cement in rotary kilns, have kept to small furnaces and complete fusion for making this cement. It would seem, however, that a combination of a rotary kiln and a reverberatory furnace, the former feeding into the latter, would unite the advantages of a rotary kiln with those of complete fusion, and some such combination may eventually be the type of plant used for aluminous cement.

Silica is almost invariably the preponderating constituent of coal ash, and since it is important to keep it out of the cement a process using producer gas instead of solid fuel would have advantages but none such appears to be in use.

As already mentioned, in the blast furnace process of manufacture the conditions are strongly reducing and metallic iron is formed if the iron oxide content of the bauxite is high. In this way iron is eliminated and it is possible to use a bauxite of much higher iron oxide content than would be permissible in the cintering process. The iron produced is low in sulphur but high in carbon, and unless it is completely separated it tends to cause trouble in the grinding of the cement. It has even been proposed [19] to make calcium aluminate from bauxite high in both iron oxide and in silica by reducing and eliminating them as ferro-silicon, but the process does not seem to be in use.

The proportion of lime or limestone and bauxite to be used depends upon their compositions. The theoretical proportion for monocalcium aluminate cement is given by the equation : Mols CaO = Mols Al_2O_3 + 2 × Mols SiO_2, or in weights : $CaO = 0{\cdot}55\ Al_2O_3 + 1{\cdot}87\ SiO_2$ (very roughly lime = half alumina plus twice silica). In actual practice the lime is always higher than these proportions indicate, so that some 5 : 3 calcium aluminate must be present. There seems to be no definite minimum to the lime content but too little yields a weak cement and one of too

high a melting-point for ease of manufacture. Furthermore, since lime is ordinarily much cheaper than bauxite, as high a lime content as possible is desirable for economy. The upper limit to the lime content is set by the properties of the cement—too rapid a set and unsatisfactory strength being the result of too high a lime content. The range of composition of commercial cements is given in the next section and the proportion of lime to bauxite is easily calculated knowing the compositions of these two constituents and allowing for the ash of the fuel used.

Grinding is an expensive item in the cost of production owing to the hardness of the fused slag and even of the clinker from a rotary kiln. It is usual to grind the slag in two stages with magnetic separation of the iron following the first stage, and it is necessary to use manganese steel liners and balls in the tube-mills employed, although flints have been found suitable.

It has been said that it takes three times as much power to grind aluminous cement slag as that absorbed in grinding Portland cement clinker to the same fineness. The efficiency of grinding has, however, been improved and aluminous cement is seldom ground as finely as Portland so that it is improbable that the difference in power consumption is now so wide. Probably aluminous cement needs about twice the power of Portland.

To overcome the grinding difficulty Voisin [13] suggests controlling the composition of the slag or clinker so that the unstable silicate is formed which reverts to the γ-form on cooling (see p. 73) with consequent disintegration of the mass. He finds that to produce this effect the cement should contain over 25 per cent. of alumina and silica between 0·4 and 0·5 of the alumina, whilst the lime must be 3 to 3·25 times the silica, and it must be cooled slowly. Using SiO_2 : 15 per cent., Al_2O_3 : 30 per cent., CaO : 45 per cent., Fe_2O_3 : 10 per cent., he obtained a clinker which spontaneously pulverised to a powder passing 180 mesh

and which set satisfactorily. The objection is that the limits of composition mentioned do not furnish a satisfactory aluminous cement. It has been found, too, that in general cements that dust do not give as high a test as those which are burnt sufficiently to prevent dusting.[23]

Another suggestion [14] is to heat the finely ground and intimately mixed raw materials together at temperatures too low for fusion for a long enough period to bring about combination. Six hours at 1000° to 1100° is mentioned, but generally much longer heating is necessary. The cement is easily pulverised and another advantage claimed is that the composition may vary much more than when the cement is fused, e.g. between the limits : SiO_2, 0–5 per cent. ; Al_2O_3, 40–55 per cent. ; Fe_2O_3, 10–25 per cent. ; CaO, 20–40 per cent. Heating may be carried out in a tunnel or rotary kiln. It has been suggested [15] that by keeping the lime low (CaO equal to or less than $\frac{1}{2}(SiO_2 + Al_2O_3)$) aluminous cement may be made like Portland cement at temperatures from 1200° to 1500°. None of these suggestions has hitherto been employed commercially, the process used in America being distinctive in that the clinker is almost as hard as the completely fused slag.

It has been proposed [31] to use bauxite instead of sand with calcium phosphate in the electric furnace method of phosphorus manufacture, aluminous cement being produced as a by-product.

Type of Bauxite Required

The bauxite for aluminous cement production should be low in silica, contain a moderate percentage of iron oxide and be low in other impurities. The important figures are the ratios of the various impurities to alumina. Cements being made to-day have the following range of composition :

Alumina (Al_2O_3)	36 per cent. to 44 per cent.
Lime (CaO)	39 „ „ 44 „ „
Silica (SiO_2)	5 „ „ 10 „ „
Iron* (calculated as Fe_2O_3)	8 „ „ 11 „ „
Titanium Oxide (TiO_2)	1 „ „ 5 „ „

* Iron occurs sometimes wholly as Fe_2O_3 and sometimes as lower oxides and as the metal.

In general the silica should be not more than one-fifth of the alumina and the iron oxide not more than one-fourth, unless it is eliminated in the manufacturing process. Limestone or lime practically free from iron oxide and low in silica can always be obtained, the silica content not exceeding 1 per cent. The lime therefore introduces not more than 0·4 per cent. of silica to the cement. Silica introduced with the fuel is a variable quantity depending on the ash content of the latter. It must be determined in each instance and allowed for. Thus if the fuel ash contains 50 per cent. SiO_2 and the fuel contains 8 per cent. ash the silica is 4 per cent. of the weight of the fuel. If the latter be 40 per cent. by weight of the cement it introduces 1·6 per cent. of silica which with, say, 0·4 per cent. for the lime totals 2 per cent. If, therefore, we aim at a limit of not more than 7 per cent. of silica in a cement containing 38 per cent. alumina the ratio of silica to alumina in the bauxite must not exceed 5 : 38. Therefore, if the bauxite contains, say, 55 per cent. alumina the silica must not exceed 7·2 per cent. It will often be found that a lower limit than this is necessary, and frequently silica is introduced from the lining of the furnace employed for fusion or cintering.

Too much silica results in cement of unsatisfactory strength and to " dusting " of the clinker or slag, which again adversely affects the setting properties. Cement burnt in a rotary kiln must generally be lower in silica than cement completely fused because the former dusts much more readily than the latter. Thus commercial rotary

kiln cement generally contains about 5 per cent. of silica whilst the fused cement has from 7 per cent. to 9 per cent.

If excess of iron oxide is eliminated as metallic iron there would seem to be no limit to the allowable iron oxide content of the bauxite, but as the iron oxide increases the alumina diminishes and since it is the ratio of silica to alumina that is the limiting factor as regards silica, the percentage of silica in the ore must diminish as iron oxide increases. There are considerable deposits of aluminous laterite low in silica which at present are practically valueless but which some day may be used as raw material for aluminous cement. In processes where the iron oxide is all retained in the cement it is preferable that it should not exceed about one-quarter the percentage of the alumina so that bauxites with percentages of ferric oxide up to about 12 per cent. are suitable.

Little is known about the effect of titanium oxide in cement but bauxites fairly high in that constituent are being used successfully in cement production. Treating it purely as a diluent the quantities generally found in bauxite will not have very much effect on the properties of the cement. There are seldom any other constituents of importance in bauxite.

Bauxites are often rather variable in composition. It is important in aluminous cement manufacture that the supply is reasonably uniform. Localised irregularities are a characteristic of this ore and one advantage of the rotary kiln process is that blending of the ground bauxite is possible so that a uniform powder may be obtained from a not too irregular ore supply. This is by no means so easy when the ore is used in lump form and in general it may be said that in the latter instance a more uniform bauxite is necessary. Blending the cement after grinding is a frequent practice to smooth out irregularities in the properties such as setting time which are mainly due to unevenness of composition.

To summarise, it may be said that bauxite for aluminous cement manufacture may be higher in iron and silica than that used for aluminium, the allowable limits varying, being dependent upon the process used and on the lime and fuel available. A bauxite that is not quite good enough for use in the Bayer process would do for cement and very roughly it may be taken that the permissible silica and iron oxide contents are double the limits generally fixed for ore used for aluminium manufacture. The ores actually used at present vary considerably : from a low silica ore containing 15 per cent. to 25 per cent. of iron oxide to an ore containing about 10 per cent. of silica and 20 per cent. to 30 per cent. of iron oxide.

Properties and Uses

As previously explained, aluminous cement was first produced as a hydraulic cement resistant to the attack of saline waters, but the property which now makes it important industrially is primarily that of rapid hardening. The statement is generally made that these cements attain as great a strength in 24 hours as Portland cement reaches in 28 days : a statement well substantiated when applied to the ordinary grade of Portland cement but not always correct if used in comparing aluminous cement with the more carefully made high lime Portlands now obtainable and sometimes referred to as " super-cements." No other hydraulic cement will give the early strength of aluminous cements and they provide a solution to many previously insoluble engineering problems, where concrete construction is indicated but where there is a time limit too short for the use of Portland cement.

When aluminous cement was first placed upon the market the high lime Portlands were almost unknown. Manufacturers had made no revolutionary changes since the first introduction of Portland cement and apart from a

steady but very slow improvement in quality the only changes made were in the direction of lowering the costs of production. To the very material benefit of cement users aluminous cement has stimulated manufacturers to the production of the so-called " super " cements which, it is probable, will eventually replace ordinary Portland cement almost entirely. In addition to its high early strength aluminous cement of good quality has an ultimate strength considerably in excess of that of ordinary Portland. It was at first thought that it would have an important field of use in structures where lightness of construction was important but this field will now probably be covered by the high lime Portlands, although the ultimate strength of the best of them is not as high as that of the best aluminous cement.

The most important application of aluminous cement, then, is where great rapidity of construction is required—in repairs and alterations to buildings in use, road repairs and for the final lengths of roads being laid or relaid in concrete, and in pre-cast work where the moulds or shuttering are costly. The advantages of its use in such instances are clear, but there are also less obvious instances where by taking all factors into consideration an economy may be shown to result from the use of the more expensive cement (aluminous cements are generally from 1·7 to 3 times the price of Portland cement). The monetary value of the earlier completion of an important building, for example, may more than balance the extra cost of the cement.

Aluminous cement is of such recent introduction and it has been so much improved that it is impossible to quote figures which adequately represent the attainments of the cement being made to-day. Furthermore, although the producing companies have masses of test figures, there are not yet available, except in America, many adequate test results obtained by independent public bodies. Table V gives three sets of figures, the first of which represents the average of the results obtained by five public testing

stations in America on 1 : 2 : 4 (sand and crushed aggregate) concrete. Better results than these undoubtedly have been obtained on American aluminous cement (e.g. see Table VI, p. 89), and probably better results are consistently being obtained to-day in similar investigations but the figures are of special value in being obtained from so many independent and reliable sources. The second set of figures represents

TABLE V

COMPRESSIVE STRENGTH OF ALUMINOUS CEMENT CONCRETE

Cement made in	Concrete Mixture	Compression Strength in Lbs./Sq. Inch at			
		24 hours	7 days	28 days	1 year
America . . .	1 : 2 : 4	3,930	4,650	4,910	5,280
France [26] . . .	1 : 2 : 4	2,430	5,520	6,170	—
	see below*	6,260†	7,640‡	8,160	11,200

* 112 lbs. cement : 1⅛ cu. ft. sand : 5⅝ cu. ft. crushed aggregate. † Mean 25–48 hours, not 24 hours. ‡ Mean 4 to 7 days.

1 : 2 : 4 (sand and shingle) concrete made with cement produced in France, and the third a rather richer (about 1 : 5) concrete using crushed aggregate. They are from a reliable source and are borne out by other tests but have not the same weight as the American test figures. That is to say, they do not so unequivocally prove that the general run of French or European cements is uniformly up to the standard they represent although they gain weight from the absence of tests proving the contrary. What they unequivocally do show is that cement of this quality can be made without using exceptionally pure raw materials because analysis shows the cement to be of average composition. It therefore seems to be assured that in the future cement of this quality or higher will be made by all

aluminous cement producers because the raw materials are so costly that it will be merely economy to make the best possible product.

Aluminous cements are slow setting. The initial set generally takes place in 2 to 6 hours and with a good cement in cool climates 4 hours is usual. The final set soon follows —often within fifteen minutes—and hardening proceeds rapidly. Expansion of the cement as estimated by the Le Chatelier test is negligible, as would be expected from the entire absence of free lime. For the same fineness of grinding the porosity is considerably less than that of Portland cement, due probably to the liberation of colloidal alumina. Adhesion to reinforcing metal and to other cement surfaces is good.

Aluminous cement evolves considerable heat in setting, and owing to the rapidity with which the reaction takes place once it starts the temperature of the concrete is raised considerably. This is an important advantage in severe climates, where it is possible to use aluminous cement without artificial heat at times and in places where the frost would render impossible the employment of Portland cement.

The durability of aluminous cement in sea and other saline waters has been the subject of tests in France extending over 10 years. It was found to be unaffected where Portland and other cements were badly disintegrated. It has also been found to be resistant to peaty water which rapidly attacked ordinary concrete. However, aluminous cement is so new that necessarily the evidence is meagre, and unfortunately little is known of the chemistry of the subject. Formerly it was thought that the disintegrating effect of sulphurous waters on cement was due to the formation of calcium sulpho-aluminate ($3CaO.Al_2O_3.3CaSO_4$) and the high resistance of the low alumina natural cements of France was confirmatory, but the tricalcium aluminate that forms this compound also occurs in set aluminous cements which

do not disintegrate. Lafuma [20] found two hydrated aluminates $4CaO.Al_2O_3.12H_2O$ and $2CaO.Al_2O_3.7H_2O$ in cements, and he concludes that the former alone, which he thinks does not occur in aluminous cement, causes disintegration with sulphates, but the weight of evidence is against the existence of any hydrated aluminates other than the tri-calcic compound. Portland cement is distinguished by its content of free lime when it is set, which moreover forms comparatively large crystals, and it would seem that the expansion of these crystals on being converted into sulphate causes disintegration in some instances. Although it has been shown [30] that the resistance of the cement increases with increasing alumina content the mere presence of free lime cannot be a determining factor because it has been shown that calcium aluminate hydrolyses in water, ultimately leaving pure alumina, and the water permeating through aluminous cement concrete has been shown [21] to contain free lime. Until more certainty is reached in these matters it will be necessary to use caution in assessing the value of aluminous cement in resisting chemical action. It has achieved some success in chemical works and Orthaus [24] has given some particulars of its application in towns gas works where resistance to sulphate liquor is necessary, and it is constantly being employed for concrete required to resist sea and other water containing magnesium salts.

The chief disadvantage attending the use of aluminous cement is the extra care necessary in handling and mixing it. It is very sensitive to certain impurities, especially lime and Portland cement, small quantities of which make it fast setting and decrease enormously its set strength. Special care is therefore necessary to ensure absence of contamination. It would also appear that some or all aluminous cement is adversely more affected than Portland cement by excess of water in mixing. Table VI, for example, sets out results that have been given [22] as representing the strength of 1 : 2 : 4 concrete after 24 hours made with American

aluminous cement. Nevertheless, in spite of this loss of early strength, the evidence is, at least with some aluminous cements, that at about 7 days most of the lost strength is

TABLE VI

COMPRESSIVE STRENGTHS IN LBS./SQ. INCH AT TWENTY-FOUR HOURS OF CONCRETE MIXED WITH DIFFERENT PROPORTIONS OF WATER

Water : Cement Ratio (by weight) . .	0·70	0·80	1·00	1·25
Compressive Strength Lbs./Sq. Inch .	5,250	4,470	3,260	1,810

recovered. This is in direct contrast to the behaviour of Portland cement, which loses strength permanently through over-watering. However, since aluminous cement is generally used for its high early strength, it must be concluded that the correct proportioning of the water is at least as important as with Portland cement. Aluminous cement concrete requires more thorough mixing than that made from Portland cement.

Some trouble has been experienced in hot climates due to the heat accelerating the set of the cement (Bolomey [32] says that the setting time increases with increase of temperature but this is certainly not the usual behaviour) and adversely affecting its strength, and also by the use of too rich mixtures of the cement where again the heat developed in setting, being insufficiently dissipated by the aggregate, causes a weakening of the mass. Again, the heat of setting tends to evaporate water from the concrete near the surface and it is necessary to wet it during setting.

Feret [33] found that the deterioration of some aluminous cement concrete in sea water was due not to attack by the water but to overheating of the mass during setting due to its having been mixed in hot weather and to the size of the masses of concrete which rendered dissipation of the interior

heat very slow. Except, possibly, in tropical countries these heating difficulties are of minor importance.

There is evidence that the strength of some aluminous cement reaches a maximum after a few months, or even less,[27] and then begins to fall off. On the other hand tests over many years have proved that it can and does often increase in strength continuously and apparently indefinitely. The rather inconsistent results are probably to be attributed partly to the variability of the cement produced in the early days of its manufacture and partly to lack of exact knowledge as to its use, and properly made cement may be expected to increase in strength continuously.

When subjected to heat sufficient to dehydrate it, aluminous cement concrete retains much more of its strength than Portland cement concrete and the dehydrated cement is less disintegrated by water. This has a certain value in reducing the risk of collapse of concrete structures in a fire. It also renders aluminous cement of value as a refractory cement, and this application of it has received attention in France and elsewhere. Arnould [25] found that a mixture of 1 part of aluminous cement and 2 parts of bauxite (dehydrated at about 1100°) has good strength. When heated to the temperature at which the water of combination is lost it becomes friable but still retains considerable strength, and on further heating to 1250° all friability is eliminated. It softens at 1350° to 1400° and fuses at 1600°. It can be used alone as a mortar or mixed with crushed firebrick to form concrete. It is very resistant to sudden change of temperature. Arnould also found that a mixture of aluminous cement with magnesite (calcined at 1000°) and waterglass is a good refractory cement but it sets too rapidly. The author has used aluminous cement with dead burnt magnesite finely ground with good results and without any noticeable acceleration of the set. It is an excellent bonding material although there is some shrinkage at high temperatures. Aluminous cement made by clinkering often

gives better results as a refractory because of its lower lime content and higher melting-point and the electric furnace fused cement may be equally good.

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CHAPTER X

ALUMINA REFRACTORIES

Refractory Properties of Alumina and Bauxite

ALUMINA, both pure and in the impure form resulting from the ignition of bauxite, is a highly refractory substance. When pure it melts at 2050° or higher and bauxite, even when comparatively impure, has a melting-point well above the temperatures experienced in most furnaces other than those heated by the electric arc. Moreover, as compared with most other refractory substances alumina is chemically inactive. It is neither strongly acidic like silica nor strongly basic like magnesia, and it is therefore well adapted to resist a variety of furnace conditions.

A good refractory must have sufficient strength when cold, and at its working temperature it must not shrink nor expand unduly nor must it crack nor spall at the working temperature or below and it must not react chemically with nor absorb any furnace charge with which it comes into contact.

Fused alumina is nearly ideal in meeting these requirements but it is very expensive and for most purposes it is usual to employ a refractory made of bauxite which has been dehydrated and heated to a high temperature. Bauxite refractories have in the past had the reputation of shrinking badly under heat. Dehydrated bauxite has a highly porous structure and its porosity is reduced at high temperatures by shrinkage. Moreover, apart from the pore space, alumina increases in true density at high temperatures.[1] If, therefore, the bauxite is not fully shrunk at a temperature higher than that at which it is to be used the refractory will shrink when in use, but if, on the other hand, it has been fully shrunk at a sufficiently high temperature no shrinkage troubles should be experienced. Diaspore shrinks less than bauxite and consequently it is preferred for refractory use where it is available.

The shrinkage of bauxite is a phenomenon that has not

been thoroughly examined. When the ore is heated it first evolves water, becoming more porous than before. Shrinkage commences at a bright red heat and continues up to high temperatures and the polymerisation (*c.v.* p. 44) which causes an increase of true density is superimposed on the shrinkage caused by decrease of porosity. Bigot [4] found that a dehydrated siliceous white bauxite (Al_2O_3 : 69·2 per cent., SiO_2 : 21·6 per cent., Fe_2O_3 : 3·4 per cent., TiO_2 : 5·7 per cent.) on heating started to shrink at 800° and continued to do so up to 1360°, very rapidly after 1200°. Above 1360° it remained stationary up to 1750° when it again started to shrink and continued to do so up to its melting-point of about 1900°. Red bauxite (Al_2O_3 : 69·2 per cent., SiO_2 : 3·3 per cent., Fe_2O_3 : 21·2 per cent., TiO_2 : 4·7 per cent.), on the other hand, shrank rapidly from 1000° to 1500° forming corundum crystals, and it fused at about 1700°. From these experiments it is clear that ferric oxide reduces the melting and shrinkage points of bauxite more than silica but there is a whole range of ores intermediate in composition between these two the behaviour of which cannot be predicted with any certainty. It would seem from Bigot's investigation that a low-iron siliceous bauxite shrunk at a temperature above 1360° would be an excellent refractory for any temperature up to 1700°, but unfortunately shrinkage is not entirely absent between these temperatures. It is slow but generally quite enough to cause shrinkage in the refractory during prolonged use.

Aluminous clay, which may contain as much as 50 per cent. of silica, is used for refractories which are sometimes called " bauxite " refractories. Such clay, whilst it makes an excellent refractory for certain purposes, is quite distinct from true bauxite in shrinkage and in other properties.[2]

As early as 1856 Deville made crucibles of alumina and a few years later the use of bauxite for a similar purpose was suggested, but it is only in the present century that bauxite refractories have been used extensively.

Fused Alumina Refractories

Fused alumina refractories are made by melting alumina —sometimes pure but generally in the impure form of bauxite—in an electric furnace of the arc type. The material used, pure alumina prepared by the Bayer or the Deville-Pechiney process or fairly pure bauxite, is first calcined at a high temperature to drive off all combined water. It is then fused and the molten material allowed to solidify, generally in the furnace itself (see Chapter XIV for further details). The block of alumina is broken up, crushed and ground and after grading it is bonded with a small percentage of kaolin or other ceramic bonding material, pressed into shape and baked.

This process is necessarily costly and fused alumina refractories command a high price. They are much used on a laboratory scale, for small industrial installations (especially electric furnaces) which require a high-class refractory, and as saggers in the ceramic industry. Such refractories are sold under several trade names such as "Alundum," "Aloxite," etc. They are often produced in two grades, from pure alumina (over 98 per cent.) and from bauxite (about 95 per cent.).

The thermal conductivity of fused alumina refractories is several times that of fireclay refractories and at high temperatures it is greater than all other refractories except silicon carbide.[8] They are therefore well adapted to use in muffle furnaces, but they are attacked by basic vapours such as those of lime and magnesia which combine with the surface layer of the alumina and scale off on cooling.

Fused alumina in powder form mixed with a small amount of bonding material is used as a refractory cement in high-class furnace work.

To lessen the cost of these refractories it has been suggested that fusion should be accomplished in a cupola. The suggestion is to use a bauxite of low to moderate silica content and fuse it with admixed coke fuel, the alumina-

silica-iron oxide slag being tapped off into moulds and annealed in the same way as blast-furnace slag paving blocks are cast and annealed, or crushed and used in the usual manner. The obvious difficulty of obtaining satisfactory fusion in a cupola of the very high melting-point mix that would be necessary for a high class refractory has not yet been overcome.

Bauxite and High Alumina Refractories

Bauxite and high alumina refractories may be defined as those refractories other than the fused alumina refractories already dealt with in which dehydrated and shrunk bauxite or diaspore is the predominating constituent. They are made by heating bauxite or diaspore clay to a high temperature, grinding it, pressing it into bricks or blocks with a binder (generally clay) and baking at a high temperature. To produce a high class block capable of withstanding a high temperature without shrinkage or other failure it is necessary to use a sufficiently pure bauxite and shrink it at a temperature well above that at which it is to be used. The rate of shrinkage of bauxite is a function of the temperature and it increases rapidly with increase of temperature. If the refractory is to be subjected to a temperature of, say, 1400° it is necessary to use a bauxite pure enough to remain hard at that temperature. To shrink such an ore at a rate fast enough for practical purposes it would be necessary to heat it well above 1400°, perhaps to 1600°. The purer the bauxite the higher the temperature required, and the higher the temperature at which the resultant refractory may be used. Manufacturers have in the past paid insufficient attention to the shrinkage of the ore before use and this is the reason for the bad reputation of many bauxite refractories. There has been a tendency merely to heat the ore to a temperature above that at which it would be used without ascertaining whether this was sufficient to bring about the necessary shrinkage, the assumption being that

if it did not shrink at this higher temperature it would not do so at the working temperature. This, however, leaves the time factor out of consideration, and in actual fact prolonged heating under working conditions causes gradual shrinkage and failure. It follows that too pure a bauxite should not be used for refractories to withstand moderate temperatures, otherwise the cost will be unduly high owing to the high temperatures required for shrinkage. In the best bauxite refractories for high temperatures the ore is said to be shrunk in an electric furnace, but it is not clear whether this expensive process gives better results than cheaper methods such as shrinking in a cupola. The usual practice is to shrink in a cupola of the same type as that used in dolomite shrinkage, raw bauxite and coke being charged in at the top and the shrunk ore withdrawn at the bottom.

Having thoroughly shrunk the bauxite or diaspore it is next crushed. Here it must be remembered that the ultimate purpose is to press the crushed ore to a block with as few voids as possible. The aim should therefore be to crush it to form an aggregate of different sized pieces in such proportion as to leave the smallest possible void space when compressed together. It is exactly the same problem as that of producing the best possible crushed aggregate for concrete. Refractory manufacturers have given insufficient attention to this : hence the tendency for the bricks to absorb slags.

The shrunk bauxite is mixed with a binder which may be clay, sodium silicate, magnesia, or other bonding material, and pressed into shape. As little binder as possible should be used consistent with giving a proper bond and not leaving the block too porous. If the shrunk bauxite has been properly sized 10 per cent. of kaolin should be enough, and probably less could be used, especially if high pressure is employed in forming the block. Kaolin is the binder most used and on the whole most satisfactory. Alsson [3] uses bentonite instead of plastic clay and finds that 5 per cent. is sufficient.

The blocks are dried and fired at a temperature well in excess of that at which they are to be used. If properly made, shrinkage is very small and distortion almost absent and the bricks or blocks are of almost perfect shape.

Refractories of all compositions between a true bauxite and a fire-clay refractory are made using an aluminous clay or mixing ground bauxite with fireclay. The concern here is with the true bauxite refractories in which clay is used only as a binder.

Type of Bauxite Required

The type of bauxite necessary varies with the duty required of the refractory. In the past it has been usual to employ bauxites high in silica on account of the strength and low porosity of the resulting refractory after it has been baked, and such ores together with aluminous clay are still used more than any others in making high alumina fire-bricks. A low silica bauxite with an iron oxide content dependent upon the temperature at which it is to be used makes a good refractory and it is being used at the present time, but such ores find a ready market in the aluminium and cement industries and consequently they generally command a higher price than siliceous bauxites. The effect of titanium has not been investigated but there appears to be no disadvantage in a moderate percentage of this constituent. Diaspore is largely used for aluminous refractories in America, and in general it may be said that bauxites which most nearly resemble diaspore (i.e. those with the least combined water) are the most suitable because they are denser and require less shrinkage before use. The Mediterranean or "terra rossa" bauxites are therefore better adapted to refractory manufacture than the lateritic ores.

Fused alumina refractories are made with moderately pure bauxite or diaspore and with alumina prepared by the Bayer or other process from bauxite (see also Chapter XIV).

Properties of High Alumina Refractories

The properties of bauxite or high alumina refractories naturally depend on their composition but in general they are highly refractory, resistant to basic slags such as those in basic steel furnaces, lead furnaces, etc., and to the clinker in cement kilns, and they retain considerable strength at high temperatures. Unless made from thoroughly shrunk bauxite or preferably from diaspore and properly graded and bonded they may be porous and permit slag penetration, and also they may shrink on long heating, but the best refractories are not subject to these disabilities. Spalling and abrasion are moderate or low, again depending on the care used in manufacture. It has been shown [5] that many bauxite refractories exhibit plastic failure at temperatures much below those at which there can be any softening of the actual bauxite, due to the fusion of the bonding material. This effect can be reduced to a minimum by properly grading the bauxite aggregate (grog), by using the least possible quantity of bonding material and by firing at a high temperature.

The spalling loss of bauxite and other bricks has been measured [6] by heating to 1350° and cooling in an air blast 10 times. It was found to be less than that of magnesia, silica, chrome and all but the best fireclay bricks. Abrasion was also measured at 1350° by rubbing against a carborundum grinding wheel. It was found to be less than all but the best carborundum bricks. However, it is impossible to say how far these results are applicable to the general run of bauxite refractories.

Bodin [7] measured the strength of 1 cm. cubes of various refractories including bauxite (Al_2O_3 : 61·1 per cent., SiO_2 : 13·3 per cent., Fe_2O_3 : 4·7 per cent., loss on ignition : 16·4 per cent.) fired at 1300° and 1500°. As with fireclay, corundum, carborundum and silica, bauxite decreases in strength at first (up to about 700°), then increases up to a maximum at 900°, after which it again falls off.

Uses

High alumina refractories are used for the linings of metallurgical furnaces, cupolas, etc., when the slag formed is neutral or basic, and in general furnace work where a high temperature is used. They are used to replace magnesite in basic steel furnaces and in many other instances. They are employed to a considerable extent in the hot zone of Portland cement kilns, especially those in which the high-lime cements are made. There is some difference of opinion about their use in ordinary cement kilns, some cement burners saying that they do not take the cement coating well. It seems probable that it is a question of temperature because there seems little doubt as to their superiority over other refractories in the high-lime cement kilns, in which a higher temperature is used. Probably their greater refractoriness and lesser chemical reactivity demands a higher temperature for the formation of an adherent coating.

The use of high alumina refractories for lime kilns has been the subject of some discussion. Their relatively high cost rules them out except for lining a limited portion of the kiln—where the temperature is highest. They have been tried in this high temperature zone but without any very definite results, and there is little reason to suppose that the lime would not flux with them in view of the ready reaction in aluminous cement production.

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CHAPTER XI

OIL REFINING

The Function of Solid Agents in Oil Refining

CHARCOAL, fuller's earth, certain clays and other substances have long been used for decolorising and deodorising mineral oils and also animal and vegetable oils, fats and waxes. Although it has for many years been known in a general way that this action is connected with a special cellular or porous structure of the solid, the exact nature of the effect was not studied until comparatively recently and it is still rather obscure. Most of the refining agents, in the terminology of colloid chemistry, are inorganic gels (partially dehydrated hydrogels), and whilst the study of these substances is still in a very incomplete state even less is known about the oil itself. It seems certain that most crude mineral oils are not simple liquids—they are emulsions or suspensions—but the nature of the motor spirit and burning oil fractions is not yet clear.

The serious study of the action of solid refining agents on petroleum products dates from 1912 when Gurwitsch [1] studied the filtration and fractionation of petroleum by a porous medium and Guiselin and Haudricourt [2] published the results of their study of the action of fuller's earth on crude and refined mineral oils. They showed that this earth absorbs all oil, but unsaturated, coloured and high density hydrocarbons are the more tenaciously held, replacing more saturated fractions. A lengthy investigation by Gilpin and Schneeberger [3] on the diffusion of petroleum through fuller's earth showed that this agent preferentially absorbs sulphur, nitrogen and unsaturated compounds.

Since then the technical side of the problem has been greatly advanced and numerous investigations have been made on the use of Florida earth, silica gel, bauxite and other similar agents without very much advance on the theoretical side except, perhaps, in the case of bauxite.

Bauxite as a Refining Agent

The use of bauxite as a refining agent is of recent growth but in many refineries it is now an important agent for the treatment of burning oil fractions and it is also used in refining other fractions of the oil.

Raw bauxite, in spite of its frequent porous nature, has little or no value as an absorbent of the undesirable constituents of petroleum fractions. It has to be heated to about 400° fully to develop its refining value and it is necessary to use it soon after ignition, otherwise its activity is decreased owing to reabsorption of moisture. Bauxites have the advantage over most similar agents of being comparatively hard and suitable for use in granular form. They are therefore well adapted to the process of filtering the oil to be refined through beds of the ore similar to the sand beds used in water filtration. It has been found [4] that for desulphurising burning oil a product ranging from 30 mesh to 60 mesh (to the linear inch) is the most effective, whilst a finer product is better for decolorising, but in both instances the optimum size probably varies with the nature of the bauxite.[5]

The behaviour of bauxite has been fairly thoroughly studied by Dunstan, Thole and Remfry [4] whose investigation points to its effect normally being two-fold—a preferential absorption of the unsaturated and sulphur-containing compounds in the oil and a catalytic effect on the former. Unsaturated (coloured) compounds are removed first and sulphur compounds are not greatly reduced until nearly all the colour is eliminated. The catalytic effect is seen to best advantage in a cracked spirit where the rate of formation of gummy polymerised compounds is enormously increased, and since after formation they are absorbed and eliminated, bauxite is an effective refining agent for cracked motor spirit.

The necessity of using the ore fresh from roasting is

emphasised by Dunstan, Thole and Remfry's work [4] and confirmed by that of Guiselin.[5] The former authors, in fact, found that by roasting the ore in a vacuum and admitting the oils without breaking the vacuum (i.e. without admitting air to the roasted bauxite) activity was extraordinarily enhanced. The sulphur was reduced to a very low percentage and catalytic activity was much increased.

The bauxite is regenerated after use by removing the entrained oil and roasting with excess of air. Its activity seems to be unimpaired by repeated use and regeneration but it is gradually disintegrated, forming a fine dust which must be removed by sifting.

Whilst bauxite is exceptionally well adapted to the removal of some sulphur compounds it is in general less effective than Florida or other fuller's earth for colour removal, and since the latter must precede the former, consecutive filtration through floridine and bauxite may be more effective than treatment with either agent alone.[6]

The general practice is to carry out the treatment at temperatures not much above atmospheric but O'Brien [7] has shown that sulphur is more effectively removed as the temperature increases up to 100°. Coloured compounds, however, are less effectively removed above about 30°, and at high temperatures the colour may actually be increased. Nevertheless, it has been shown [4] that treatment at a high temperature polymerises or otherwise changes the coloured compounds so that they are more easily removed by subsequent treatment at low temperatures. This effect is even more pronounced when the oil vapour is passed over heated bauxite, and cracked spirit is said to be rendered absolutely stable and sweet smelling by such treatment.[8]

Precipitated alumina, dehydrated to the correct degree, is very active as a refining agent, being superior to the best bauxite or fuller's earth as a decolorising agent,[9] but it does not seem to be used commercially.

Type of Bauxite Required

Little is known relative to the type of bauxite most suited to oil refining and it is unfortunate that the work done on the subject has not been planned to reveal more data on the nature of the activity of the agent bauxite. It is known in a general way that the more highly hydrated ores are more effective than ores containing little combined water and that heating to about 400° and not much above is necessary for high activity. At this temperature there would be little, if any, dehydration of the monohydrate whilst gibbsite would be reduced from the trihydrated to the monohydrated condition or almost to the anhydrous state (see p. 46). It would seem likely that it is the colloidal hydrated alumina when partially dehydrated that is most effective as a refining agent, and if this is so a bauxite of high combined water content that has the smoothest heating curve (with the least marked " arrest points ") would have the greatest efficiency. Experimental evidence on this point is lacking.

In the absence of any definite information the only reliable guide is an actual test of any particular ore. Dunstan, Thole and Remfry [4] found that the temperature rise on adding an oil (preferably kerosene) to the freshly dehydrated bauxite is a reliable guide to its value as a refining agent and they proposed a simple apparatus [10] which they call an " ergometer " for the test, in which 200 c.c. kerosene is added to 500 g. freshly ignited bauxite, and the rise of temperature measured.

It is fairly safe to say that a high combined water content is desirable and not too high a percentage of iron oxide and from the fact that Indian ores are used successfully it would seem that titanium oxide is not detrimental. Since clays are effective refining agents silica may not be a disadvantage. Hard bauxites would appear to be better than soft ones, apart from the advantage they have when the ore is to be used in granular form, but there may be very active soft ores.

Refining Processes Used

In the practical application of the bauxite refining process the ore is first granulated in a machine which will make a product all passing 10 mesh with the least possible amount of fines (— 90 mesh). It is difficult to crush to this fineness without making a considerable amount of dust and 20 to 25 per cent. is usual.[7] The granular ore is next roasted in a small rotary kiln at a temperature of 400° or over. Normally the kiln is engaged in regenerating used bauxite to which a small amount of new material is added to make up for losses as dust, etc., and an oxidising atmosphere is employed to burn any carbonaceous matter out of the pores of the ore. The bauxite must be cooled out of free access to the atmosphere to prevent reabsorption of moisture, and generally it is delivered direct to the treatment plant by enclosed metal conveyors which may be water cooled.

The treatment plant varies in different refineries.[12] In its simplest form it consists merely of a large cylindrical tank with a grid near the bottom on which rests a gauze or cloth or both supporting the bauxite which nearly fills the tank. The quantity of oil capable of being refined by this bauxite is found by a laboratory test and this amount is run through. The oil held by the ore is reduced to a minimum by suction or steaming or both and the bauxite, which now contains absorbed sulphur-bearing and coloured oily compounds, is returned to the kiln for regeneration.

This simple procedure may be modified by employing a number of filters in series, the filters being recharged in turn and the oil flowing first through the oldest filter. Such an arrangement results in a larger volume of oil being treated by a given weight of bauxite and also in a more uniformly refined oil. Another modification results from the adoption of the suggestion [6] already mentioned to use Florida earth and bauxite consecutively. Bauxite too fine for the filtration process may be used by the method of

agitating it with the oil—a process often employed when using argillaceous refining agents.

The rather cumbersome process of regeneration in a rotary kiln is costly and the excessive handling involved makes a great deal of fines. O'Brien mentions a much simpler process in which regeneration is carried out in the filter itself by the introduction of superheated steam at 350° or over, which, in spite of the high cost of the steam, results in a very considerable economy of operation. It would seem doubtful whether regeneration by this process could be used many times without a considerable decrease of activity because the carbon would not all be removed from the pores of the bauxite, but possibly kiln regeneration is carried out after several steam treatments. It is not clear why hot furnace gases are not used instead of superheated steam. With a treatment plant of suitable construction they could be employed without any trouble at a much less cost than using steam, and they would have the same regeneration effect as kiln roasting.

Vapour phase treatment of cracked spirit has been carried out by Gray [11] and although he used fuller's earth the same effect would be obtained with bauxite. The Gray process is designed to operate continuously with a cracking still. The vapour from the still passes up an outer column and down through an inner column filled with the fuller's earth or bauxite. Near the bottom of this inner column there is a pipe to lead off the vapour to the condenser and a run-off for the polymerised products which condense in the column.

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CHAPTER XII

SULPHATE OF ALUMINA

Introductory

ALUMINIUM sulphate and its compound with potassium sulphate, alum, have been known and used from the earliest times, mainly as mordants in dyeing. They occur native to a limited extent in arid regions and were originally obtained from such deposits and later from alunite or alum-stone, an insoluble basic hydrated sulphate of potash and alumina, $KAl(SO_4)_2.2Al(OH)_3$. On calcination alunite loses water and the sulphates are rendered soluble, leaving behind alumina. It is still used as a source of alum but workable deposits are rare and the process of extraction slow and it competes with difficulty with alum made from bauxite.

Aluminium sulphate has now replaced alum for most commercial purposes. It is a more concentrated and a cheaper source of hydrated alumina—the effective agent in nearly all the applications of these chemicals. Alum is the more easily purified and it is therefore still employed where high purity is essential.

Aluminium sulphate is made by dissolving bauxite or pure alumina in sulphuric acid and evaporating off excess water, and alum by adding the appropriate quantity of potassium sulphate to the sulphuric acid solution before evaporation.

Type of Bauxite Required

In the process of making sulphate of alumina from bauxite iron oxide is dissolved and silica remains inert. It is therefore desirable to use a bauxite low in iron oxide, and siliceous ores, unsuitable for most other uses, are widely employed. The white bauxites of France have long been used for this purpose. There are, however, no bauxites so low in iron oxide that they will directly yield a product sufficiently low in iron for many industrial applica-

tions of aluminium sulphate, and since processes of freeing the solution from iron have not proved commercially successful it is usual to employ pure alumina for the preparation of the iron-free salt. This alumina is made by the dry or the wet process described in Chapter VIII and the bauxite used must be low in silica whilst its iron oxide content may be fairly high. Consequently two types of bauxite are used in the sulphate of alumina industry, the low-iron high-silica type and the low-silica high-iron type.

The siliceous bauxites used for direct solution in acid should contain less than 5 per cent. of iron oxide and often the limit is set at 3 per cent. The silica may have almost any value as long as the soluble alumina is sufficiently high. If the silica is not combined with the alumina it has no effect on the reaction and its presence merely involves the handling of a larger quantity of sludge from the acid solution of the ore, but in general the silica in a siliceous bauxite is partly combined with the alumina to form kaolin. Kaolin is inert to acid but on dehydrating it at about 600° the alumina is rendered soluble and the available alumina in a siliceous ore is often increased by calcining it. However, it is not as readily soluble as the free alumina and the necessary calcination increases the cost of the whole process so that ores with a high combined silica content are seldom used at present, although they may come into greater use in the future. That such bauxites could be used industrially is shown by the fact that sulphate of alumina is still made from kaolin to a limited extent.

The bauxite used for preparing pure alumina for iron-free sulphate may be high in iron oxide and the silica need not be as low as it must be when the alumina is to be employed in the manufacture of the metal. This is because there is seldom any objection to the presence of a small amount of silica in aluminium sulphate, and if there were it could be removed by letting it settle out of the acid

solution of the precipitated alumina. For the same reason the dry (Deville-Pechiney) process is often used to make alumina for this purpose.

Processes of Manufacture

As already indicated there are two distinct processes of manufacture—the direct process for " alumino-ferric " (a mixture of aluminium and ferric sulphates) and for the slightly ferruginous but white salt and the indirect process for the pure iron-free salt. In the direct process the low-iron bauxite is dried and finely ground, preferably to pass 100 mesh. Some bauxites, especially if they contain much silica as kaolin, are preferably calcined before use. The ground bauxite is mixed with sulphuric acid of specific gravity 1·35 to 1·5 (45 per cent. to 60 per cent.), or sometimes higher. Details vary considerably in different plants but the treatment vessel is preferably a lead-lined boiler which may be tightly closed when the bauxite and acid have been introduced. Injected steam serves to stir and heat the mixture and once the reaction starts heat is evolved and the pressure in the boiler rises. The reaction is complete in 10 to 20 minutes, after which the pressure sinks. If a closed boiler is not employed there must be means of removing the steam and acid fumes evolved during the reaction, and more dilute acid is often employed to moderate its violence. The solution is diluted, generally to about S.G. 1·30 (measured hot), and allowed to settle. Settling is slower with some ores than with others and this is an important point in selecting a bauxite for this purpose. The clear solution is evaporated to anything from S.G. 1·35 to 1·55 (measured hot) and run into shallow iron or lead-lined cooling tanks, which are generally divided so that the salt is obtained in blocks.

Depending on the iron content of the bauxite and on the purity required in the sulphate of alumina the evaporation

is carried to varying stages. By evaporating only to S.G. 1·35–1·40 only part of the aluminium sulphate crystallises out on cooling and, especially if reduced to the ferrous condition, nearly all the iron sulphate remains in solution. The crystallised sulphate may be pressed at high pressures to remove the iron-containing mother liquor and in this way a sulphate suitable for most purposes other than dyeing may be prepared. The mother liquor may be evaporated to produce "alumino-ferric" (sulphate of aluminium containing a considerable amount of ferric sulphate) or it may be employed to produce potash alum which is easily purified from ferrous iron by re-crystallisation. If "alumino-ferric" for water and sewage purification is to be made evaporation is carried much further and on cooling the liquor completely solidifies. The solid lumps are generally crushed before sale.

Many processes have been suggested for the removal of iron from the bauxite solution. It may be precipitated as Prussian blue by oxidising it all to the ferric state with bleaching powder and adding the required amount of ferrocyanide. The Prussian blue is filtered off (filtration is difficult) and reconverted into ferrocyanide. Another process precipitates a basic ferric potassium sulphate [1] and there are others,[2] but none of them is used commercially to produce an iron-free sulphate. They are occasionally used to reduce the iron content of the liquors.

Recent improvements [3] embody continuous operation in which ground bauxite, strong acid and weak wash liquors are fed in regulated streams to the first of three covered agitators of the Dorr type, lined with lead and with silicon-iron agitating mechanism. Their combined capacity is sufficient to give ample time for complete reaction, and they feed from one to the other by overflow. Steam is injected for heating. The final overflow from the last reaction tank passes into a large thickener from which clear liquor overflows whilst the thickened residue is washed in two other

thickeners in series. The clear liquor is evaporated. Other modern plants employ a slightly different arrangement but the principle is the same.

In the indirect process alumina is first prepared from bauxite by the Bayer or the Deville-Pechiney process. The latter process is still used to a considerable extent in this industry (see page 56 for details of the process). The precipitated alumina is washed and drained thoroughly but not dried. It is stirred into sulphuric acid of S.G. 1·65 to 1·80 or even stronger, depending on the quality of sulphate required, using a little less than the theoretical amount of acid necessary to give $Al_2(SO_4)_3$. The mixture froths up but on the completion of the reaction it subsides and the liquid is run into shallow lead-lined pans to solidify. Partitions may be put in the pans to facilitate breaking up the mass or it may be stirred during solidification to reduce it to small lumps. Depending on the strength of acid used, etc., the salt may contain anything from 14 per cent. to 16 per cent. Al_2O_3.

Alums

" Alum " is a term used generally for compounds of the formula : $M^{\cdot}M^{\cdots}(SO_4)_2.12H_2O$ (where $M^{\cdot}$ is an alkali metal or ammonium and $M^{\cdots}$ is usually aluminium, chromium or ferric iron) and particularly for potash or " common " alum $KAl(SO_4)_2.12H_2O$. The only alums of commercial importance are potash and ammonia alums. Soda alum was formerly used to some extent but it is very soluble and difficult to crystallise so that it has no advantage over the cheaper and more concentrated aluminium sulphate.

Potash and ammonia alums are made by adding potassium and ammonium sulphates in calculated proportion to solutions of aluminium sulphate, evaporating and crystallising out. If the solution is ferruginous some chloride may be employed to convert the iron into the very

soluble ferric chloride and prevent its crystallising out with the alum. Both alums are only sparingly soluble at ordinary temperatures and have steep solubility-temperature curves (especially potash alum) and as they crystallise well from solution they are particularly well adapted to purification by re-crystallisation.

The alums have the same uses as sulphate of alumina and in addition they are used in medicine. Potash alum is also used for domestic purposes and in the preparation of certain gypsum plasters, particularly Keene's Cement.

Uses

Nearly all the uses of sulphate of alumina and of alum depend on the property possessed by colloidal alumina of absorbing other colloids and holding them with extraordinary tenacity. Its most important uses are in the dyeing and colour making industries, in the treatment of water, sewage and other effluents and in paper making, and it also finds application in leather manufacture, the preparation of "satin white," and in making other compounds of aluminium.

In dyeing sulphate of alumina is employed as a mordant. The textile is soaked and often boiled in a solution of the salt, sometimes with the addition of a base to assist in the separation of the hydrated alumina, which is adsorbed to the textile fibres. The material is then boiled in a bath of the dye which, in turn, is adsorbed to and fixed by the alumina. In this way dyes which do not colour or are easily washed out of textiles when used by themselves are permanently fixed to the fabric, and such dyes include many of the best and fastest. Nearly all the natural dyestuffs must be used with a mordant. For delicate dyestuffs the salt must be practically free from iron.

The "lake" colours, which are widely employed in paints, distempers, wall-paper printing, etc., are coal tar or

natural dyestuffs adsorbed to precipitated alumina, barium sulphate, tannin, etc. Nearly all the acid colours are precipitated with alumina or with a mixture of it with barium sulphate, and alumina precipitated with lime is often used with the red azo colours. The dye in aqueous solution is added to the alum or aluminium sulphate solution and the hydrate is thrown out by adding a base. The precipitate is carefully washed and dried.

Water, sewage and other effluent treatment with sulphate of alumina or " alumino-ferric " depends on the property of precipitated alumina of carrying down with it large quantities of organic matter which is in colloidal solution in the water. A strong solution of the salt is thoroughly mixed with the water or sewage when, if the latter is alkaline, alumina is precipitated together with the organic matter from the water. If the water is neutral or acid, lime or sodium aluminate may be added to bring about precipitation. The precipitated alumina and organic matter is filtered off, leaving a clear pure water. Finely divided inorganic matter is also carried down. This use of ferruginous aluminium sulphate has grown very rapidly and is continually on the increase. One application is to the continuous purification of the water in swimming baths. It is possible to keep the water perfectly clear and (with the simultaneous use of a little chlorine) absolutely aseptic for a cost that in many places works out at less than the cost of changing the water as frequently as is usual.

In paper making aluminium sulphate is used in sizing the paper. Rosin size (rosin dissolved in sodium carbonate solution) is added to the pulp in the beater and then a solution of aluminium sulphate added, precipitating rosin and hydrate of alumina, probably partly in combination, on the cellulose fibres. This industry absorbs a large proportion of the sulphate made.

Satin white is a mixture of hydrated alumina and calcium sulphate. It is prepared by the interaction of

milk of lime and aluminium sulphate solution under exactly controlled conditions of temperature, dilution, etc.[4] The sulphate must be very low in iron to furnish a good white.

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CHAPTER XIII

OTHER COMPOUNDS OF ALUMINIUM

Sodium Aluminate

Sodium aluminate, often prepared by the dry (Deville-Pechiney) process is used for water treatment and dyeing in place of, or in conjunction with, aluminium sulphate. It may be used in treating slightly acid waters without any other reagent and with aluminium sulphate it forms an excellent precipitant for neutral or nearly neutral waters. Its use by itself and as an adjunct to sulphate has been discussed by Barnitt and Haux [1] and by Powell.[2] It may be used by itself with bicarbonate waters on which it has a softening effect. Used with sulphate it hastens the precipitation and therefore reduces the size of the plant required and flocculation is better in cold water, and it reduces acidity and therefore corrosion, or alternatively reduces the consumption of soda ash.

In dyeing it is employed as a mordant for acid dyes and with aluminium sulphate in the manufacture of lakes.

The aluminate for water and sewage treatment may be simply the crude cinter, from heating together bauxite and sodium carbonate, finely ground to facilitate its solution in water. The presence of the insoluble impurity is immaterial as it is thrown down with the other precipitate. For dyeing a pure aluminate solution must be employed. It may be prepared by the dry or the wet process and the aluminate liquor, after filtering off the insoluble sludge, may be evaporated to high concentration for transport.

Aluminium Chloride

Aluminium chloride has come into considerable prominence in recent years and there has been much investigation into methods for its cheap production. In its important uses it is required in anhydrous condition and unfortunately the anhydrous salt cannot be prepared from the aqueous

solution or from the hydrated crystalline salt because it is hydrolysed and hydrochloric acid is evolved in preference to water. An aqueous solution of the chloride is readily prepared by dissolving bauxite or pure alumina in hydrochloric acid. It has been suggested to prepare the chloride free from iron from ferruginous bauxite by dissolving in hydrochloric acid and precipitating aluminium chloride by saturating the solution with hydrochloric acid gas.[3] The iron chloride remains in the mother liquor.

The anhydrous chloride is made by acting on metallic aluminium with dry hydrochloric acid gas at a high temperature, by heating bauxite or alumina with carbon in chlorine gas or by some modification of these methods. There have been many patents [4] taken out on methods of preparation, but few of them are of much interest. One that should be valuable [5] proposes treating a mixture of alumina or bauxite, carbon and metallic aluminium in powder form with chlorine. The heat generated by the action of the gas on the metal is sufficient to effect the reaction between the alumina, carbon and chlorine. The problem of uniformly heating the charge in the presence of chlorine—difficult to carry out on account of the low thermal conductivity of the alumina-coke mixture and the chemical activity of the chlorine—is thus solved by the heat being generated in the charge itself. The container need not be a good thermal conductor and an iron retort lined with carbon (coke and pitch) is suggested. Whatever process is used the chloride is vaporised and condenses as a white or coloured crystalline mass of hexagonal scales, which fumes in air with evolution of hydrochloric acid. It must therefore be kept in air-tight containers.

Aqueous aluminium chloride is used to a limited extent for " carbonising " wool. The anhydrous salt [14] is a very effective catalyst of organic reactions and is used as such in many commercial organic syntheses. Friedel and Crafts [6] first showed the effectiveness of the salt in bringing about

organic condensations, and the type of reaction named after them has been very fertile in providing new organic compounds both in the laboratory and on a plant scale. The tonnage used for these purposes is small but since the introduction of the process of cracking on a large scale in the petroleum industry anhydrous aluminium chloride has been used as a catalyst of the cracking reactions. The cracking or pyrogenesis of petroleum or its fractions consists of the breaking up of the large molecules of the oil to produce lower boiling point compounds. The aim in cracking is to convert kerosene and gas oil into motor spirit and the difficulties encountered are the tendency to overcrack with the production of uncondensable gas (a tendency that is increased with rising temperature) and the unstable and unsatisfactory nature of the product, which in general consists largely of unsaturated compounds which tend to polymerise and form gummy products. Commercial cracking processes generally employ high pressure to overcome, in part, these disabilities. Catalysts have been suggested but it was not until McAfee [7] introduced the use of aluminium chloride that any commercial success was attained with these agents. Briefly the effect of aluminium chloride, which is simply suspended as a powder in the oil being heated, is to reduce the temperature necessary for the break-up of the large oil molecules and also to induce combination with the unsaturated compounds formed, producing stable compounds. A lower temperature may be employed, atmospheric or a low pressure only is necessary and very little fixed gas is produced. The process is or was used commercially and it seems to be agreed that it would be very widely employed if aluminium chloride could be produced and recovered at a low enough price. The salt is soon rendered inactive and recovery from the carbon which remains in the still as a result of the cracking is not easy.

Another drawback is that unless the oil is perfectly dry its water content hydrolyses the chloride, rendering it

inactive and the hydrochloric acid liberated attacks the apparatus.

Straight cracking without using a catalyst has been so much improved in recent years that it seems unlikely that there will be much room for the McAfee process for making ordinary motor spirit, but it is widely applicable and it may be used in the future in making other products, either simpler or more complex, from petroleum oils.

Aluminium Acetate

Aluminium acetate is made by the action of acetic acid on freshly precipitated alumina or by the action of aluminium sulphate on lead or calcium acetates or on acetic acid and calcium carbonate.[8] It is used in pharmacy, in water-proofing fabrics and as a mordant for certain dyes. For reasons not properly understood some dyes are carried down with the alumina from the acetate but not from the sulphate, e.g. fast green, acid green and croceine orange.[9] In water-proofing fabrics they are dipped alternately in sodium soap and the acetate solutions, aluminium soap being precipitated on the fibres.

Aluminium Oleate and Stearate

Aluminium oleate and stearate are made by the interaction of aluminium sulphate and sodium oleate and stearate, or sometimes by combining the acids with gelatinous alumina. The oleate is used in pharmacy,[15] as a water-proofing agent and particularly for thickening or increasing the viscosity of lubricating and other oils. The stearate [16] is employed in the paint industry for flat-finish paints and as an emulsifying agent.

Bauxite and Alumina as Catalysts

It is convenient in this chapter to mention briefly the application of bauxite and alumina as catalytic agents. The

catalytic activity of bauxite on certain compounds in motor spirit and burning oil has already been mentioned (p. 102) and it is an active agent in many organic reactions. Precipitated alumina or alumina gel, however, has even wider application. It is used particularly in the conversion of ethyl alcohol into ethylene, a reaction that has been studied considerably,[10] and also of alcohol into ether.[12] Ethylene is likely to be of some industrial importance in the future. It was used on a large scale in the production of mustard gas and quite recently it has been found to have a marked effect in accelerating the ripening of fruit. Alumina is also an effective organic condensing agent.[11] Alumina gel has most of the properties that have made silica gel of industrial importance but it has been less investigated. It is claimed by Lecesne [13] that bauxite can replace platinum as a catalyst of gas reactions.

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CHAPTER XIV

ALUMINA ABRASIVES

Alumina Abrasives

The alumina abrasives include corundum, emery and the various artificially prepared pure alumina products. Corundum, which is crystalline alumina, ranks next to diamond in hardness, and emery is corundum mixed with hematite or other impurity. Corundum occurs in the Transvaal, Canada, India and the United States, and emery is obtained in Greece, Asia Minor and the United States. These minerals are mined, washed or otherwise purified, crushed and classified into products of varying fineness. They are used in dust or grain form, as a coating on paper or cloth and cemented together to form abrasive wheels and stones. Natural corundum and emery were formerly the best abrasives known, and although their place has been very largely taken by fused alumina abrasives they are still used in some countries and for certain special processes. For example, none of the artificial abrasives has hitherto been found suitable for polishing glass, and natural emery is still almost exclusively used for this purpose. Fused alumina abrasives have been produced since the beginning of the century. They are employed in steel and other metal grinding and polishing, and are more efficient than silicon carbide in grinding metals of high tensile strength. Their properties, too, can be varied more to suit special conditions and compared to the natural abrasives they are of more uniform and dependable quality. They are marketed under several trade names such as " Alundum " and " Aloxite."

The properties of importance in an abrasive are hardness, toughness and mode of fracture. The hardness of fused alumina apparently is not altered much by changing its composition within the range actually used in practice but its toughness is widely variable and controllable. Its toughness and its mode of fracture cause it to grind tough

metals efficiently and evenly. Silicon carbide, the other widely used artificial abrasive, is brittle and in grinding tough metal it constantly fractures forming jagged edges which score deeply into the metal surface but do not grind evenly and efficiently.

Process of Manufacture

The process of manufacture is simple. It consists of smelting a mixture of bauxite of the right quality, coke and iron borings in an arc furnace of simple form. The furnaces are movable, being mounted on cooled tracks, and they consist of a steel frame lined with firebricks or unlined and with a carbon hearth. The steel sheath may be water cooled and it may be in two sections, the top half being removable. The fused mass solidifies on the lining and protects it from fusion. Furnaces of both circular and rectangular sections are employed. The mixture of bauxite, coke and iron is put in the furnace to a depth of about one foot, the vertical electrodes placed in position and a train of graphite laid between them to start the arc. As the mixture is melted more is added until the furnace is full when it is removed and allowed to solidify. The silica and iron oxide are reduced in the process, forming ferro-silicon, and enough iron is added to keep this below 15 per cent. silicon, so that on breaking up the ingot the ferro-silicon is separable magnetically (a higher silicon alloy is too weakly magnetic). Furnaces generally operate at about 100 volts and the power consumption may be anything from 2000 to 4000 K.W.H.s per ton of abrasive, the figures quoted in the literature varying widely. Complete reduction, such as is aimed at when producing pure alumina for metal manufacture by the Haglund process, is not desired because the abrasive is then too brittle. Two per cent. to 3 per cent. of silica, titanium oxide and iron oxide is desirable and generally the titania varies from 1 per cent. to 2 per cent. whilst the silica and

iron oxide are comparatively low. Too much reduction also results in the production of aluminium carbide which is said to cause disintegration of the abrasive, and it has been proposed [1] to substitute metallic aluminium for carbon as a reducing agent to obviate this. It is not clear how volatilisation of the metal would be avoided. Each " run " of a large furnace occupies about 30 hours and produces a " pig " of 5 tons or more. The " pig " is generally allowed to cool for several days although sometimes rapid cooling is adopted to modify the properties of the abrasive by decreasing the size of the crystals formed. It is broken into small pieces and picked over, magnetic methods generally being used to eliminate ferro-silicon, and the selected material is further crushed to produce the various sizes of grain used industrially.

Type of Bauxite Required

The bauxite used is generally of a quality inferior to that required for metal manufacture and it is possible to eliminate almost any amount of iron and silicon by reduction, but in practice too high a silica is undesirable because of the quantity of iron required and ferro-silicon made. Too high a titania is apparently to be avoided but there is little information available on this point, and one or two per cent. is generally favoured. Other impurities such as lime and magnesia may be added to modify the properties of the abrasive but the practice is not general. The degree of the elimination of the impurities always present in bauxite, together with control of the cooling of the pigs, generally permits sufficiently wide variation of properties. Introduction of the alkali metals also varies the properties by forming slag-like compounds with the impurities and producing striations amongst the alumina crystals.

The bauxite must be completely dehydrated before use either at the mine or at the treatment plant. This is accomplished by heating to about 1200° in a rotary or other kiln.

Artificial Gems

Rubies, sapphires, oriental amethysts and other gems consist of alumina with small quantities of colouring impurities, and they are now prepared artificially by fusing alumina in an oxy-coal gas flame. The alumina is prepared as a fine powder from pure ammonia alum and it is sifted slowly into the stream of oxygen used in the flame, which plays downwards on to a refractory flat where the fused material is caught. A pear-shaped mass of the crystalline gem is produced which is broken up into individual gems. Rubies are produced by adding a little ammonium chromium alum to the ammonium alum used and blue sapphires by adding titanium and iron oxides.

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CHAPTER XV

THE FUTURE OF BAUXITE

The Future Consumption of Bauxite

THE statistics of the world's bauxite production reveal a very striking increase in recent years. As with all similar raw materials there was an abnormally high production in the war years followed by a heavy slump, but there are very few commodities that so rapidly rose again and exceeded the war-time maximum. Furthermore there are reasons for thinking that this rapid rate of increase is likely to be exceeded in the near future. The provision that has recently been and is being made by the aluminium companies to increase production, unless it is due to over-optimism on their part, foreshadows an unprecedented increase, with a corresponding advance in the demand for bauxite. The plant recently built in Quebec, for example, will ultimately have an output of 100,000 tons a year of aluminium. Moreover a limit cannot be set to the possible increase in the production of aluminous cements. Unquestionably, the cost of their production will soon be decreased and the main item of cost will be bauxite. Their cost, and therefore the extent of their use, will consequently depend largely on the market price of the ore, and if it were possible to supply bauxite at a low enough price at cement plants in industrial countries the demand for this one purpose would soon rise to many times the present total output. However, the probability is that the price of bauxite in industrial Europe and America will increase rather than diminish as the deposits favourably situated for shipment are exhausted. Sensational increases in consumption by the other industries are unlikely but a steady growth is practically assured.

The demand for bauxite is therefore likely to increase rapidly and there are strong inducements to open up occurrences of the ore within reach of the markets.

Bauxite Substitutes

The world's resources of bauxite are not known but discoveries of the ore in recent years suggest that their exhaustion is a remote contingency. There is, however, a real danger of a serious depletion of supplies within easy access of the present points of consumption—there is already talk of prohibiting export from France and Italy—and the increased freightage from less accessible occurrences will inevitably give a strong impetus to attempts to utilise other sources of alumina. Clay is a source available almost everywhere and there is no difficulty in preparing pure alumina from it, but the alumina so prepared at present costs much more than that made from bauxite. Numerous processes have been patented all of which may be said to fall within one of two classes, namely thermal processes, in which the impurities are reduced and removed leaving pure fused alumina (the Haglund process is an example) and processes in which the alumina is dissolved in acid and precipitated or obtained by the thermal decomposition of the salt (e.g. the process [1] in which the clay is dissolved in hydrochloric acid and the chloride decomposed by calcination).

Other suggestions involve the use of alumina-containing minerals or rocks. Goldschmidt [2] found that the plagioclase felspar in Labrador stone was very soluble in dilute acids, leaving silica and iron-magnesia minerals undissolved. He proposed using 30 per cent. nitric acid as a solvent, precipitating iron, and evaporating and heating to a temperature sufficient to decompose aluminium nitrate but not calcium and sodium nitrates, which are dissolved out, crystallised and used as fertilisers. This process would seem to have achieved some success in Scandinavia, but its use as a source of alumina is obviously very limited. In Italy the Blanc process [3] is said to be used for producing

alumina and potash from leucite. It consists of a process of enriching the mineral by magnetic separation after which it is treated with hot hydrochloric acid, when potash and alumina dissolve leaving a hydrogel of silica which adsorbs any silica which may be dissolved by the acid. Potassium chloride crystallises out on cooling and aluminium chloride is thrown out of solution by gaseous hydrochloric acid gas. The chloride on heating yields alumina and hydrochloric acid gas.

In the production of sulphate of alumina raw materials other than bauxites have long been employed but they have been superseded almost entirely. Alunite is still used to a limited extent and if large supplies of that mineral of high grade were available it would probably compete successfully, but the process of treating it is slow and it has not proved a serious competitor. China clay has been used to some extent but it is unlikely to make much progress until the price of bauxite advances considerably. In America a double silicate of iron and aluminium (Pampeano loess) is dissolved in concentrated sulphuric acid to produce "alumino-ferric,"[4] but this is merely a local development.

Conclusion

It is probable that the future will see the extended use of siliceous bauxites and even of aluminous clays to produce alumina and ferro-silicon by fusion and reduction. Ferro-silicon is at present made in the electric furnace and used for deoxidising steel, adjusting the silicon content of cast iron and in producing high silicon steels (for transformer cores, etc.) and acid resisting irons. The simultaneous production of pure alumina and ferro-silicon has great possibilities, especially if it is feasible to make a high silicon alloy. At present an alloy of less than 15 per cent. silicon is generally made, metallic iron being added to reduce the silicon to this amount, because magnetic separation is difficult with any

higher silicon content, but other methods of separation are possible and will doubtless come into use.

Another development that may be anticipated is the more complete utilisation of the constituents of bauxite. The present practice of shipping raw bauxite from the mines to the aluminium or other works where it is used, often many thousands of miles distant, is uneconomical in that a considerable weight of water and impurities is shipped with it and thrown away at the treatment plant. There are uses for all the important constituents of bauxite and unquestionably, if local conditions allow it, the most favourable procedure economically would be to separate the ore into its various constituents at or near the mine, shipping the pure products to the distant consumers. By such procedure it would often be possible to use bauxite of much lower quality than at present. A siliceous and ferruginous bauxite that at present is quite valueless might, for instance, first be treated by the Deville-Pechiney process separating it into mixtures of alumina and silica and mixtures of iron oxide and titania. The former mixture could be used to produce iron-free sulphate of alumina and, by suitable treatment, silica gel of commercial value, and the latter mixture would be separated into titania and iron oxide, the former having a very high market value whilst the oxide of iron would sometimes be of use as a red pigment. Alternatively the alumina and silica might be separated by dissolving the former in hydrochloric acid and driving off the acid again by heat, leaving alumina suitable for reduction to the metal.

Progress in exploiting the full value of bauxite has in the past been hampered by the control exercised by the aluminium producers over nearly all supplies of bauxite, and with the wider ownership and freer market that now exists more rapid development is likely. With the more extended market for lower grade ore that could be opened up the cost of mining all grades would be reduced and

already some progress has been made in this direction at some of the controlled mines by shipping bauxite of too low a grade for the metal to cement works.

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